NITRATIONS With NITROGEN PENTOXIDE With SPECIAL REFERENCE To The NITRATION Of FLUORANTHENE.

By

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I N D E X.

I N T R O D U C T I O N.

Many attempts have been made to explain the mechanism of substitution in general and nitration in particular in the benzene series. One school of thought advocates the formation of an intermediate additive compound, names such as Flürscheim, Kekulé, Armstrong, and Holleman being associated with this theory; whereas Obermiller, Vorländer, and Robinson assume direct substitution. The arguments for and against have been given in great detail by the authors concerned. It is not proposed to touch on the general aspects of the problem in this thesis, but rather on one particular type of substitution reaction, namely, nitration with a mixture of nitric and sulphuric acids.

It is known that nitric acid undergoes some change in the presence of excess of sulphuric acid. Saposchnihoff (Z. physikal. Chem., 1904, 49, 697 ; 1905, 51, 609 ; 53, 225) deduced that such a change occurs from abnormalities in the vapour pressure and the electric conductivity of nitric acid in excess of sulphuric acid. He attributed it to the formation of nitric anhydride. Walden (Z. anorg. Chem., 1924, 37, 390) confirmed this view and von Halban (Z. physikal. Chem., 1928, 132, 433) attributed changes in the

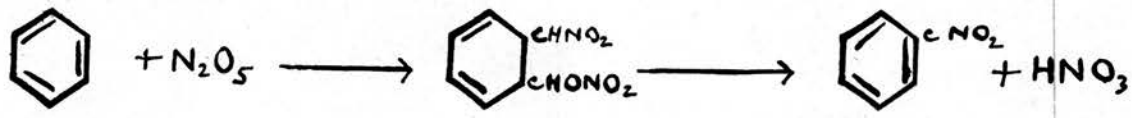
adsorption spectrum of nitric acid in sulphuric acid to the presence of nitric anhydride. Dalman, Chédin and Brissaud (Compt. Rend., 1935, 201, 664) found that the Raman Spectra of most nitrating agents showed the lines characteristic of the anhydride; while Chédin (Compt. Rend., 1935, 201, 552) noted that the Raman Spectra of nitric anhydride, dissolved in carbon tetrachloride or chloroform, differed from that of the pure anhydride. He observed the similarity of the spectra in the above solvents with that of metallic nitrites - a result which caused him to suggest the presence of the nitrite ion in a solution of nitric anhydride.

It was well known that the anhydride of nitric acid could be obtained by distilling the acid in the presence of a strong dehydrating agent, such as phosphorous pentoxide. The equilibrium can be displaced to the acid or anhydride by the addition or removal of water.

$$2HNO_3 \underset{H_2O}{\overset{P_2O_5}{\rightleftharpoons}} N_2O_5 + H_2O$$

Schaarschmidt (Z. angew. Chem., 1926, 39, 1457) alleged that the anhydride formed in a mixture of acids was the most powerful of nitrating agents. The anhydride was assumed to add on to the aromatic compound forming a derivative of dihydrobenzene which, due to its instability, rapidly decomposed.

The reaction may be represented diagramatically as follows:-



Gordon (Thesis, Edinburgh, 1937) performed a series of nitrations using nitric anhydride in solvents such as carbon tetrachloride, acetic acid, or acetic anhydride. If nitration involving a mixture of acids does proceed via the anhydride, then the results obtained from the two methods should be comparable.

Haines and Adkins (J. Am. Chem. Soc., 1925, 47, 1419) were other authors to use nitric anhydride for the purpose of substitution. Most of their work is concerned with aliphatic substitution. They did find, however, that benzene could be transformed quantitatively into nitrobenzene at 0°C., and further that nitrobenzene, to quote their report, "appeared to give a quantitative yield of m-dinitrobenzene". They could not introduce a third nitro-group into the benzene nucleus; whereas Meyer (Ber., 1889, 22, 23) claims to have obtained trinitrobenzene using sulphuric acid as solvent at 160°C. It would appear, however, that at this temperature the nitric anhydride decomposed.

No other work on these lines could be traced and

it was decided to conduct a series of nitrations with nitric anhydride in the hope that more evidence could be obtained either to support or oppose the anhydride hypothesis. A repetition of previous work showed that some of the results obtained were unreliable, and it was therefore decided to study more carefully nitrations or aromatic compounds with nitrogen pentoxide. One of the major difficulties encountered was the quantitative separation of isomers, due to the number of fractional crystallisations necessary in the course of purification. Sometimes only a partial separation was achieved. To overcome this difficulty it was attempted to apply thermal analysis to the products of nitration. Pounder and Masson (J. Chem. Soc., 1934, 1359) devised an apparatus in which it was possible to determine melting points to within 0·1°C. with small quantities of material. They used this apparatus in a study of the dinitrobenzenes. A similar apparatus was constructed, and the results obtained from it were found to be in very good agreement with those of Pounder and Masson.

The thermal analysis on the products of nitration of acenaphthene was attempted, but without success, since the melting point curve obtained for mixtures of 2- and 4-nitroacenaphthene was not the usual melting point curve, probably due to the formation of molecular compounds.

The method was applied in an exhaustive study of

the products of nitration of nitrobenzene in different amounts of sulphuric acid at different temperatures. It was not found to be practicable in the case of the nitrodiphenyls, for two reasons:- (a) the presence of traces of dinitrodiphenyl, and (b) the oily nature of the products of nitration. A recrystallisation would have been necessary to free the solid from oil. Such a recrystallisation would have rendered the results of thermal analysis useless. The method was therefore only of practical importance in selected cases, and was therefore discarded. Subsequently the nitration of a hydrocarbon, in which a directive group was already substituted, was examined under various conditions, including the case where a catalyst was added.

It was then decided to investigate the nitration products of some of the higher hydrocarbons and to determine what orientation occurred. Fluoranthene was the first such hydrocarbon to be selected. On nitration it readily and quantitatively yielded a trinitro-derivative, identified as such by analysis. Normally a complicated molecule can be disrupted into simpler compounds by oxidation or reduction, and the orientation of the simpler substances helps in elucidating the structure of the original compound. In the case of trinitro-fluoranthene, however, all attempts at oxidation or reduction failed, due perhaps to the complete insolubility of the compound.

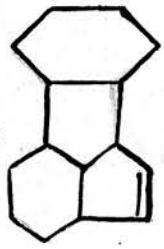
It is known that substituents already present in the benzene ring exert a decisive influence on further substitution in that ring. Substituents may be divided into three groups: A, those which aid further substitution; B, those without influence; and C, those which hinder further substitution. Some substituents are classified below:-

Group A	Group B	Group C
CH_3	Cl	NO_2
NH_2	Br	COOH
OH	I	$COCH_3$

For example, m-dinitrobenzene is not readily converted into trinitrobenzene, whereas 2:4-dinitrotoluene can be readily converted into 2:4:6-trinitrotoluene. On the other hand, benzoic acid is relatively hard to nitrate.

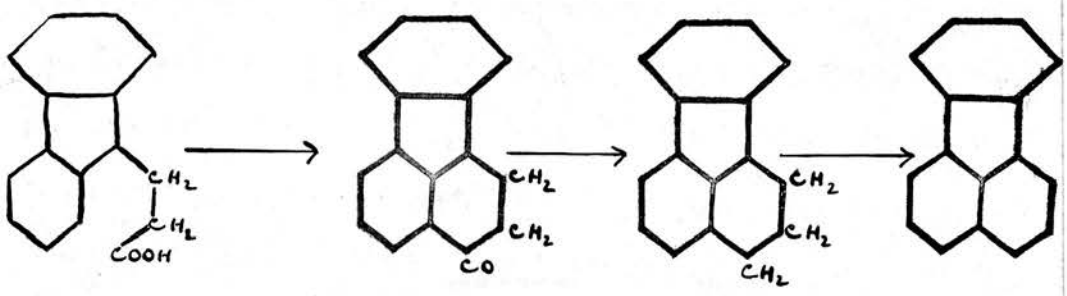
The problem was attacked from a new angle which is outlined as follows. A substituent X is introduced into the fluoranthene molecule, the position which it takes up being either known or ascertained. X is a substituent which tends to prevent the entry of a nitro-group into that particular ring. We then nitrate this compound and find out from analysis how many nitro-groups have entered the molecule. If this procedure was carried out on a sufficient number of derivatives, the position of the nitro-groups in trinitrofluoranthene would eventually be solved.

At this stage it is advisable to survey what is known of the chemistry of fluoranthene. Goldschmidt first described the isolation of fluoranthene, then called Idryl, since it was obtained along with mercury ores in Idria. Later it was found to occur in the higher boiling fractions of coal tar. Goldschmidt (Ber., 1878, 10, 2022) described some of its properties, such as the formation of a picrate, bromo-compound, and quinone. As a result of analysis and vapour density determinations, he assigned to it the formula $C_{15}H_{10}$. Fittig and Gebhard in the same journal (page 2141) supported his formula and recorded the formation of a trinitrofluoranthene, using fuming nitric acid. In the next year Goldschmidt (Ber., 1879, 11, 1578) described its isolation from the mercury ore with xylene and purification; while in the next year Fittig and Liepmann (Ann., 1880, 200, 1) described its separation from coal tar and also studied its oxidation products. They described the oxidation of fluoranthene into fluorenone-1-carboxylic acid and a quinone which formed a complex with the hydrocarbon. They also reduced the fluorenone acid to the corresponding fluorene acid. Goldschmidt (Wien. Abad. Ber., 1881, 81, 415) reported that reduction with phosphorous and hydriodic acid gave rise to $C_{15}H_{12}$ and at higher temperatures to $C_{15}H_{14}$. The following formula was assigned to fluoranthene:



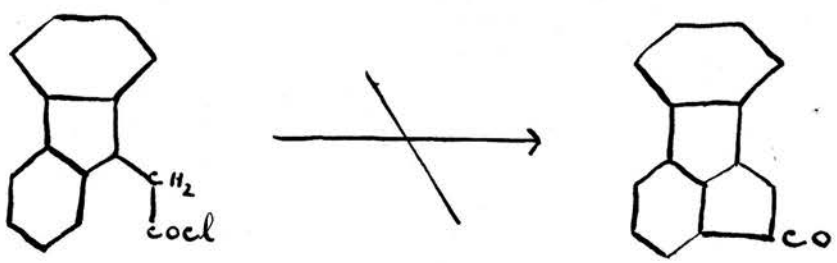
Goldschmidt (Monats., 1880, 1, 221) described the preparation of tribromo- and trichloro-fluoranthene, the preparation of the sulphonic acid, and the conversion of it via the cyanide into the carboxylic acid. Later the same author (Monats., 1902, 23, 886) followed up his previous work with a description of various derivatives of fluorenone-1-carboxylic acid, including 1-aminofluorenone from the amid amide, and 1-hydroxyfluorenone by diazotisation of aminofluorenone. A lull in the chemistry of fluoranthene followed until Anton and von Braun (Ber., 1929, 62, 145) pointed out that the conception of fluoranthene as a derivative of indene was not in harmony with their work on the stability of ring systems. The presence of one more carbon atom in the molecule would not greatly affect the analysis figures, they argued; while the observed facts could be readily explained if fluoranthene were a derivative of naphthalene rather than indene. They followed up this suggestion by the synthesis of

fluoranthene which established its constitution as a derivative of naphthalene. The synthesis may be summarised as follows: ~~ethyl~~ fluorenylpropionic acid 1 was converted into the acid chloride by means of thionyl chloride; this compound was cyclised by aluminium chloride in petroleum to give 4-keto-1:2:3:4-tetrahydrofluoranthene 2 , which, when reduced by Clemmensen's method, gave 1:2:3:4-tetrahydrofluoranthene 3 . 3 was oxidised with lead oxide to fluoranthene 4 .



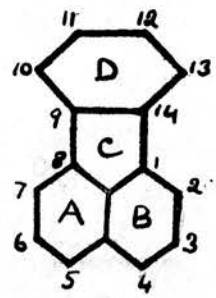
I II III IV

They also showed that fluorenylacetyl chloride, when treated with aluminium chloride in petroleum, could not be cyclised to the indene derivative.



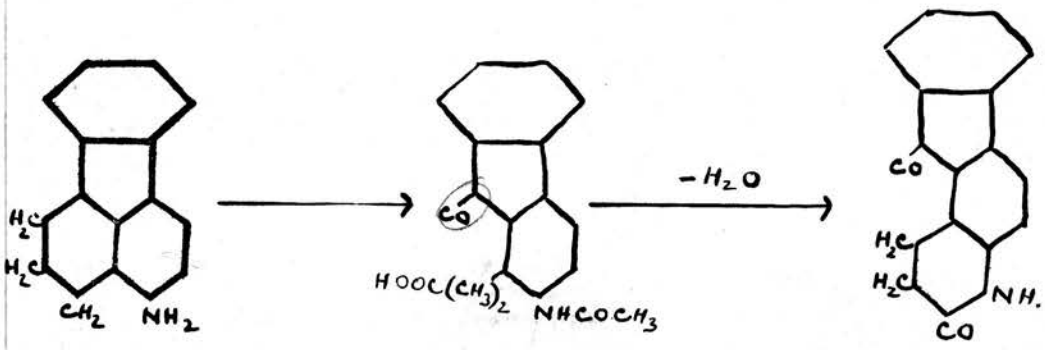
Another synthesis of fluoranthene has been effected by Cook and Lawrence (J. Chem. Soc., 1936, 1431), starting from 1-(1'-naphthyl)-2-methyl- Δ^{1}-cyclohexane.

At this stage the notation for the fluoranthene molecule, which will be the basis of all subsequent work, may be given



Von Braun and Manz (Ber., 1930, 63, 2608) studied the hydrogenation of fluoranthene and found that it occurred successively in rings B and D. 1:2:3:4-tetrahydrofluoranthene is formed, using sodium amalgam and alcohol, whereas hydrogenation with nickel in decahydronaphthalene gives rise to 1:2:3:4:9:10:11:12:13:14-decahydrofluoranthene. In the next year von Braun and Manz published the results of their work on monosubstitution (Ann., 1931, 488, 111). They isolated bromo-, nitro-, amino-, hydroxy-, cyano- and sulphonic acid derivatives of fluoranthene. There are five possibilities for monosubstitution, i.e., 2, 3, 4, 12 or 13. Guided perhaps by the synthesis of fluoranthene involving

4-keto-1:2:3:4-tetrahydrofluoranthene, von Braun suspected position 4 and was able to prove that his supposition was correct, in the following way. Amino-fluoranthene can be reduced to the 5:6:7:8-tetrahydro-derivative I, the acetyl derivative of which is oxidised to the ketocarboxylic acid II. The deacetylated acid passes readily into the lactam III with loss of water, showing that the original compound was 4-amino-fluoranthene.



I II III

The three main derivatives, bromo-, nitro-, and sulphonic acid, are readily converted to the same aminofluoranthene or the cyanide formed from it (as outlined below).

$C_{16}H_9Br \longrightarrow C_{16}H_9CN \longrightarrow C_{16}H_9COOH \longrightarrow C_{16}H_9CONH_2$

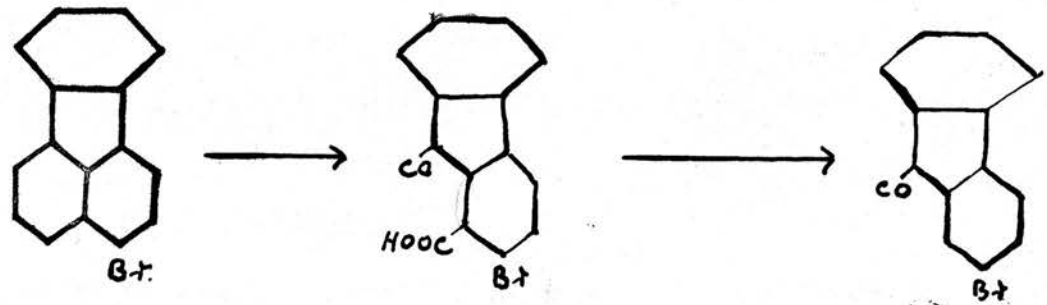
$C_{16}H_9NO_2 \longrightarrow C_{16}H_9NH_2 \longrightarrow C_{16}H_9OH$

$C_{16}H_9SO_3H \longrightarrow C_{16}H_9EtSO_2NH \longrightarrow C_{16}H_9CN \longrightarrow C_{16}H_9COOH \longrightarrow C_{16}H_9CONH_2$

$\longrightarrow C_{16}H_9OH \longrightarrow C_{16}H_9NH_2.$

The authors continued their previous work (Ann., 1932, 496, 170) by oxidising the monosubstituted nitro- and bromo-fluoranthene to the corresponding 2-fluorenone-1-carboxylic acid 1 which, when heated with soda lime,

passed into the fluorenone compound.



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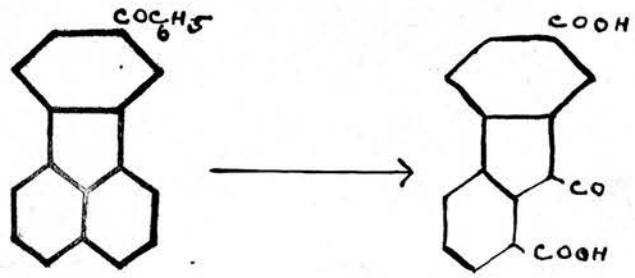
In marked contrast to the orientation of the previous derivatives was the fact that acylation of fluoranthene proceeds primarily to the 12-position, together with small amounts of the 4-derivative and diacyl derivative. Acylation to the 12-position was proved by oxidation to the fluorenone 1:7-dicarboxylic acid.



Since Goldschmidt's work was carried out prior to the alteration of the formula, his results are liable to doubt. It is for this reason that much of his work has been repeated and in some cases corrected.

Object of Fluoranthene Research.

1. Orientation of polysubstituted derivatives.

2. Preparation of simple derivatives by reasonably simple methods, e.g., 4-bromofluoranthene, 4:12-diacetylfluoranthene. Some simple derivatives, however, could not be obtained, e.g., triamino-fluoranthene and the produets of oxidation of the trinitro compound.

3. Besides the method of orientation which was applied, namely, by making use of the properties of groups in facilitating or hindering further substitution, it was hoped to apply other methods, which were found to be unpractical because of experimental difficulties; for example, if the triamino-fluoranthene had been obtained, it should condense with a 1:2-diketone, provided that the compound contained two amino groups in ortho-positions.

4. The preparation of halogen-nitro-compounds and the use of halogen reactivities in determining the orientation of the compounds.

E X P E R I M E N T A L.

The experimental work is described in the following pages. Yields of products are quoted as percentages of the maximum theoretical amounts obtainable. Melting points are corrected, the thermometer used having been calibrated against standard thermometers. All new compounds have been analysed.

Preparation of Nitrogen Pentoxide. cf. J.A.C.S., 1939, 61, 3067.

Nitrogen pentoxide was prepared by the dehydration of nitric acid with phosphorous pentoxide by a modification of the methods described by Berthelot and Weber (J. pr. Chem., 1873, 6, 342 ; Ann. Chim. Phys., 1875, 6, 202), Daniels (J. Amer. Chem. Soc., 1920, 42, 1133) and Haines and Adkins (J. Amer. Chem. Soc., 1925, 47, 1425) in an all-glass apparatus. Nitric acid was dried by distilling with phosphorous pentoxide in the ratio of four parts by weight of nitric acid (1·51) to one part of phosphorous pentoxide. Anhydrous nitric acid distilled over at 80°C. to 85°C. This acid with twice its weight of phosphorous pentoxide, which had been slowly added with external cooling to prevent rise in temperature, was heated on a water-bath. An air condenser was used and an adapter led from this into

the receiving flask immersed in an ice-salt freezing mixture. On raising the temperature of the water-bath to 60-75°C. nitrogen pentoxide slowly distilled over into the receiving flask where it solidified into a brittle yellow compound. The nitrogen pentoxide thus prepared could be stored in a stoppered bottle in a desiccator, the whole being kept in the refrigerator. The yield was about 60% of the theoretical based on the amount of acid used.

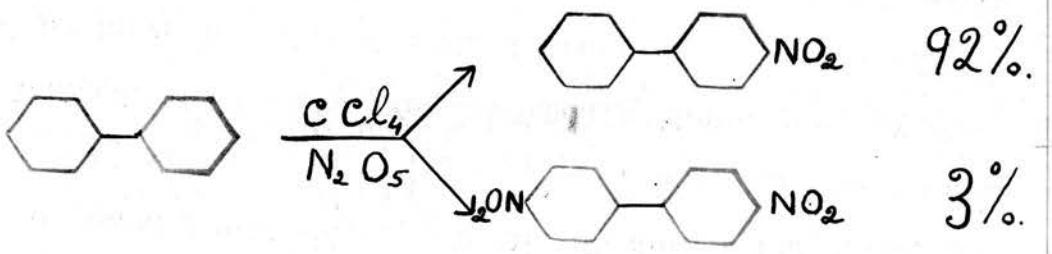
In many cases a solution of nitrogen pentoxide in a solvent such as carbon tetrachloride was used as the nitrating agent: such a solution could be kept for long periods without decomposition, was more easily handled than the solid nitrogen pentoxide, and gave a simple method of adding accurately a required weight of the nitrogen pentoxide.

Nitration of Diphenyl in Carbon Tetrachloride at 45°C.

$C_6H_5 \cdot C_6H_5 = 154$
0·13 Mol.
$N_2O_5 = 108$
0·13 mol.

Diphenyl (20 g.) was dissolved in carbon tetrachloride (45 c.c.) at 45°C. Nitrogen pentoxide (14 g.), i.e. the theoretical quantity for mononitration, was slowly distilled into the solution, the temperature being maintained at 45°C. Below 20°C no reaction occurred, while at temperatures over 60°C. the nitrogen pentoxide disintegrated. A vigorous reaction took place as each drop of nitrogen pentoxide fell into the solution. The nitrated product was left overnight and was found to have

partially solidified. The solution was filtered through a sintered glass filter and the solid washed free of nitric acid. Yield 8 g. The filtrate was shaken with water to remove nitric acid, dried over calcium chloride, and on evaporation yielded 18 g. of a pale yellow compound. The total solid was recrystallised from methyl alcohol. A small insoluble fraction yielded 1 g. of needles, m.p. 205 to 220°C. This, on recrystallisation from acetic acid, was found to be 4:4'-dinitrodiphenyl, m.p. 233°C. The solid soluble in methyl alcohol yielded 24 g. of needles, m.p. 113°C.: i.e. 4-nitrodiphenyl. Total yield 95%. Equation for the reaction:

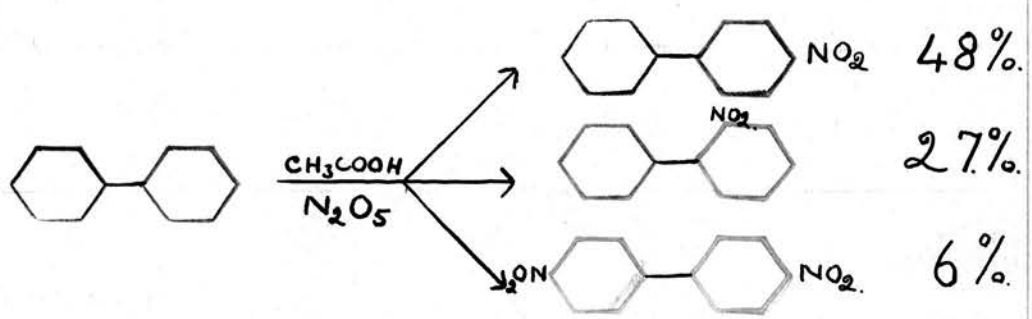


Nitration of Diphenyl in Acetic Acid at 45°C.

Diphenyl (20 g.) dissolved in acetic acid (45 c.c.) at 45°C. was similarly nitrated with nitrogen pentoxide (14 g.). The solid deposited overnight was filtered off and washed free from nitric acid, and yielded 6 g. of 4-nitrodiphenyl and 2 g. of 4:4'-dinitrodiphenyl. The acetic acid filtrate was poured into 400 c.c. of

water. A mixture of solid and oil was obtained. The former was separated by filtration, and on recrystallisation from methyl alcohol yielded a further 6·5 g. of 4-nitrodiphenyl. The oil was extracted with ether, dried, and distilled at 190 to 205°C. at 20 mm. It was then dissolved in alcohol, and water was added to bring down the oil; sufficient ether to redissolve the oil was added. On evaporation at room temperature 7 g. of solid, m.p. 37°C., were obtained: i.e., 2-nitrodiphenyl. Total yield 81%.

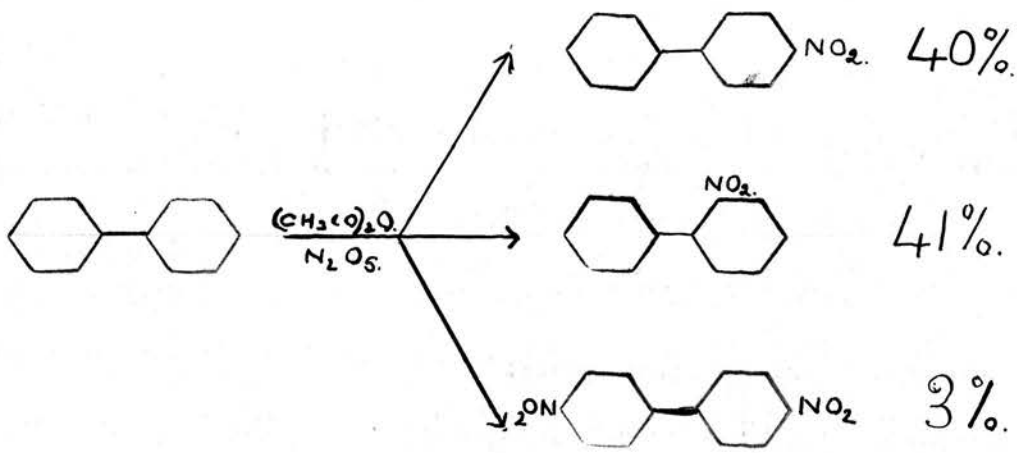
Equation for the reaction:



Nitration of Diphenyl in Acetic Anhydride at 45°C.

Diphenyl (20 g.) dissolved in acetic anhydride (45 c.c.) at 45°C. was similarly nitrated with nitrogen pentoxide (14 g.). The solid deposited overnight was separated by filtration and yielded 5 g. 4-nitrodiphenyl and 1 g. 4:4'-dinitrodiphenyl. The acetic anhydride

filtrate was washed with water and extracted with ether. The ether solution was dried over calcium chloride and then evaporated. The residual oil was distilled at 10 mm.; the main portion distilling over a range of 180 to 200°C. This was dissolved in alcohol at 40°C. On cooling, 4-nitrodiphenyl (5 g.) was deposited, m.p. 113°C. The filtrate was evaporated, and 2-nitrodiphenyl (12 g.) in the form of plates and prisms was obtained, m.p. 37°C. Total yield 84%. Equation for the reaction:

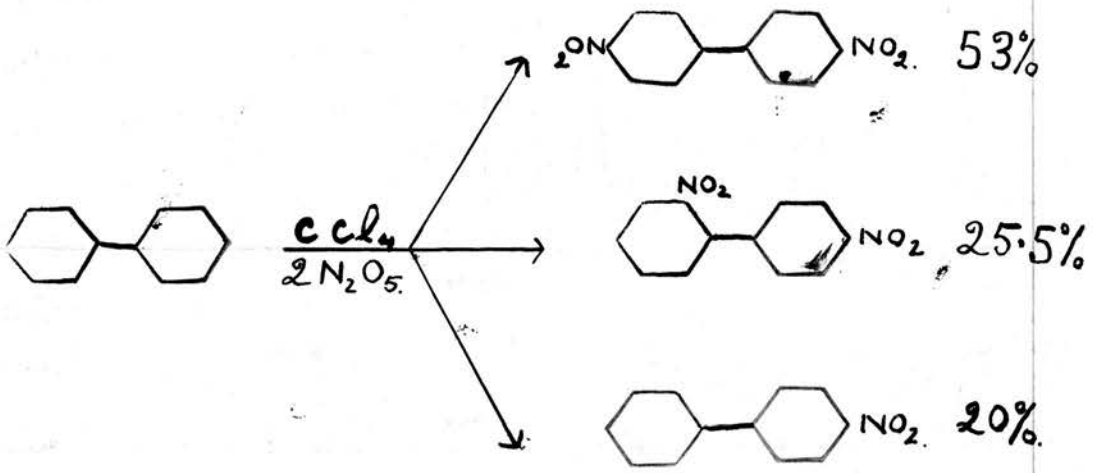


Dinitration of Diphenyl in Carbon Tetrachloride at 45°C.

Diphenyl (20 g.) was dissolved in carbon tetrachloride (45 c.c.) and nitrated with nitrogen pentoxide (28 g.). The mixture was left overnight. The solid formed was separated by filtration, washed and dried. On recrystallisation from acetic acid, 4:4'-dinitrodiphenyl (16·5 g.), m.p. 236°C., was obtained. The carbon tetrachloride layer was washed with water, dried

over calcium chloride and evaporated. The solid residue was recrystallised from acetic acid and yielded prisms, m.p. 95°C.: i.e., 2:4'-dinitrodiphenyl (8 g.). On evaporation of the acetic acid, 5 g. of 4-nitrodiphenyl, m.p. 113°C., were obtained. Total yield 98·5%.

Equation for the reaction:



Dinitration of Diphenyl in (1) acetic acid at 45°C.
(11) " anhydride at 45°C.

Diphenyl (20 g.) dissolved in acetic acid (45 c.c.) was nitrated by the gradual addition of N_2O_5 (28 g.). The solid deposited overnight was removed and yielded 4:4'-dinitrodiphenyl (8 g.). The filtrate, after being well washed with water, was extracted with ether. The ether solution was dried over calcium chloride and evaporated. The oily product was taken up in methyl alcohol. Some solid was deposited by use of the ether treatment, and this in fractional crystallisation from isopropyl alcohol yielded 2:4'-dinitrodiphenyl (8 g. approx.).

Further deposition of solid from the mother liquor was not obtained, an oil being obtained when carbon tetrachloride, ethyl alcohol, methyl alcohol or isopropyl alcohol were used. Thus, while the products of dinitration of diphenyl in acetic acid are 4:4'- and 2:4'-dinitrodiphenyl no quantitative estimation was possible.

Similar results were obtained with acetic anhydride as solvent.

Nitration of 2-Nitrodiphenyl at 45°C in

(1) carbon Tetrachloride
(11) Acetic Acid
(111) Acetic Anhydride

2-Nitrodiphenyl (20 g.) was dissolved in carbon tetrachloride (45 c.c.) and nitrogen pentoxide (10·7 g.) was added, the temperature being maintained at 45°C. The mixture was left overnight and was then poured into water. The resulting mixture was extracted with ether, the ethereal solution dried over calcium chloride and evaporated. The residual oil was dissolved in hot methyl alcohol. On cooling, 2 grammes of solid, which on further crystallisation yielded 2:4'-dinitrodiphenyl (2 g.), were isolated. The filtrates were concentrated and the oil was recrystallised from petrol ether, methyl alcohol, ethyl alcohol, isopropyl alcohol, or carbon tetrachloride. 2:2'Dinitrodiphenyl (2 g.), m.p. 124°C., (Proof ?) was obtained from the isopropyl alcohol recrystallisations,

but separation on a quantitative basis was impossible. Nitration of 2-nitrodiphenyl thus gives rise to 2:2'- and 2:4'-dinitrodiphenyl.

Similar results were obtained when acetic acid or acetic anhydride was used as solvent.

Nitration of 4-Nitrodiphenyl in Carbon Tetrachloride at 45°C.

4-Nitrodiphenyl (9 g.) was dissolved in carbon tetrachloride (45 c.c.). Nitrogen pentoxide (4·8 g.) was added at such a rate that the temperature was maintained at 45°C. The solid deposited overnight was separated by filtration, washed free from nitric acid, and dried. 4-:4'-Dinitrodiphenyl (8 g.) was obtained on recrystallisation from acetic acid. The carbon tetrachloride filtrate was shaken with water to remove nitric acid, and extracted with ether. The ether solution was dried over calcium chloride and evaporated. The residual oil, after several crystallisations from methyl alcohol, gave a mixture of needles and prisms, m.p. 70 to 80°C. Ethyl alcohol, petrol ether, and benzene were used unsuccessfully as solvents for recrystallisation. A separation, however, was effected by crystallisation from isopropyl alcohol, when prisms of 2:4-dinitrodiphenyl (2·7 g.), m.p. 94-5°C., were obtained. Thus the isolation of 2:4'-dinitrodiphenyl unsuccessfully attempted by Gull and Turner (J. Chem.

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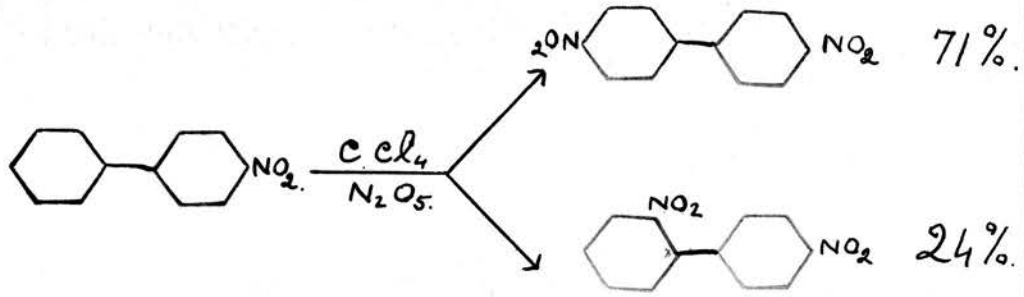
Soc., 1929, 2, 494) was effected. Gordon (Thesis, Edinburgh, p. 68) claims to have obtained 96% of 4:4'-dinitrodiphenyl when 4-nitrodiphenyl was nitrated in carbon tetrachloride. Total yield 95%.

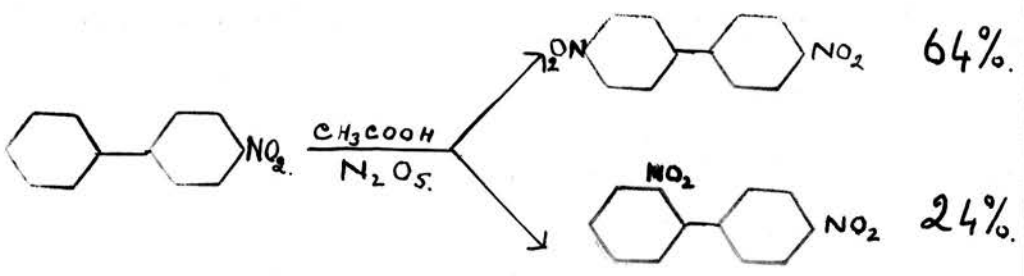
Equation for the reaction:



Nitration of 4-Nitrodiphenyl in Acetic Acid at 45°C.

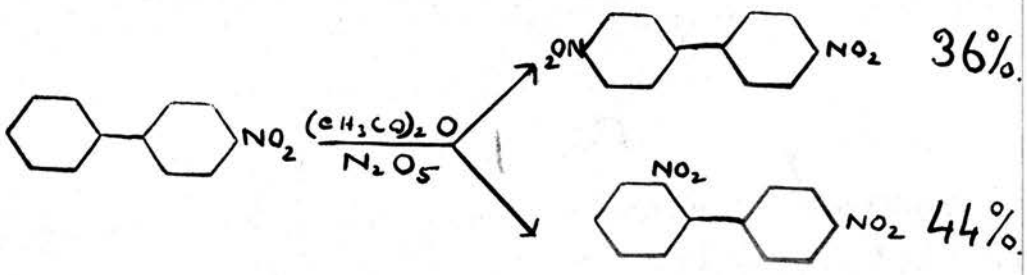
4-Nitrodiphenyl (9 g.) was dissolved in acetic acid (45 c.c.), and nitrogen pentoxide (4·8 g.) was added. The solid deposited overnight was removed by filtration and recrystallised from acetic acid to give 4:4'-dinitrodiphenyl (5 g.). The filtrate was concentrated and yielded 2·4 g. of the 4:4'-dinitro compound. The filtrate was further evaporated on the steam-bath. The residual oil was recrystallised from isopropyl alcohol and yielded 2:4'-dinitrodiphenyl (2·7 g.), m.p. 95°C., in the form of prisms. Total yield 88%.

Equation for the reaction:



Similarly the nitration of 4-nitrodiphenyl (9 g.) in acetic anhydride (45 c.c.) produced 4:4'-dinitrodiphenyl (4 g.) and 2:4'-dinitrodiphenyl (5 g.). Total yield 80%.

Equation for the reaction:



Identification of 4-Nitrodiphenyl by reduction to the Amine and Acetylation.

(Scarborough and Waters, J. Chem. Soc., 1927, 1, 91)

A solution of 4-nitrodiphenyl (3·7 g.) in ethyl alcohol (30 c.c.) was refluxed for 3 hours with a solution of stannous chloride (24 g.) in concentrated hydrochloric acid (24 c.c.). The alcohol was distilled off and, on cooling, the amine was deposited as the double salt. The free amine was liberated by treating the double salt with excess 50% sodium hydroxide. The amine was extracted with ether and deposited yellow leaflets, m.p. 50 to 52%, as the ether evaporated. For further confirmation the amine (1 g.) was treated with acetic anhydride (2 c.c.) containing two drops of concentrated sulphuric acid. On adding the cooled solution

to water the white acetyl compound was deposited, m.p. 168°C., and crystallised from ethyl alcohol in needles, m.p. 171°C. (lit., 171°C.).

Similarly 2-acetylamidodiphenyl, m.p. 118°C., was prepared. (lit., 119°C.).

Identification of 4:4'-Dinitrodiphenyl by reduction to the Diamine and Acetylation.

4:4'-Dinitrodiphenyl (1 g.) was suspended in concentrated hydrochloric acid (10 c.c.) and ethyl alcohol (2 c.c.). A few pieces of tin were added, and the solution refluxed until clear. The clear liquid was decanted and treated with sufficient 30% sodium hydroxide to redissolve the precipitated stannous hydroxide. The amine was extracted with ether and deposited as leaflets, m.p. 120°C., as the ether evaporated. The amine was acetylated and yielded the pale grey 4:4'-diacetamidodiphenyl, m.p. 317°C. (lit. 319°C.).

Similarly 2:4'-diaminodiphenyl, m.p. 45°C., and 2:4'-diacetamidodiphenyl, m.p. 202°C., were prepared (lit. 202°C.).

Similarly 2:2'-diaminodiphenyl, m.p. 161°C., and 2:2'-diacetamidodiphenyl were prepared (lit. 161°C.).

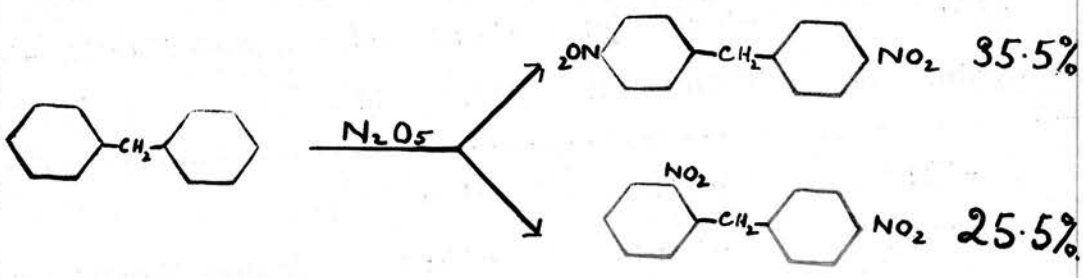
Nitrations in the Diphenyl Series.

	CCl_4	CH_3COOH	$(CH_3CO)_2O$
Diphenyl (mononitration)	92% 4-	48% 4-	40% 4-
	3% 4:4'-	27% 2-	41% 2-
		6% 4:4'-	3% 4:4'-
	95% Total	81% Total	84% Total
Diphenyl (dinitration)	53% 4:4'-	4:4'-	4:4'-
	26% 2:4'-	2:4'-	2:4'-
	20% 4-	No quantitative separation.	
	99% Total		
4-Nitrodiphenyl	71% 4:4'-	64% 4:4'-	36% 4:4'-
	24% 2:4'-	24% 2:4'-	44% 2:4'-
	95% Total	88% Total	80% Total
2-Nitrodiphenyl	2:2'-	2:2'-	2:2'-
	2:4'-	2:4'-	2:4'-
	No quantitative separation		

Dinitration of Diphenylmethane without a Solvent.

Nitrogen pentoxide (30 g.), representing 2·1 molecular proportions, was slowly added to diphenylmethane (20 g.) contained in a flask surrounded by an ice-salt freezing mixture. A vigorous reaction took place, and

the temperature of the mixture rose and remained at 45°C. The product solidified on standing. It was well washed with water to remove nitric acid, and dried. The solid was shaken with ether and filtered. This solid was insoluble in alcohol and was crystallised from benzene, yielding 11 grammes of pale yellow needles, m.p. 183°C.: i.e., 4:4'-dinitrodiphenylmethane. The ether soluble fraction was fractionally recrystallised from alcohol, yielding 3 grammes of needles, m.p. 118°C.: i.e., 2:4'-dinitrodiphenylmethane. On complete evaporation of the alcohol an oily solid was obtained, which when dried in vacuo, yielded a further quantity of 2:4'-dinitrodiphenylmethane (5 g.). Total yield 61%. Equation for the reaction:

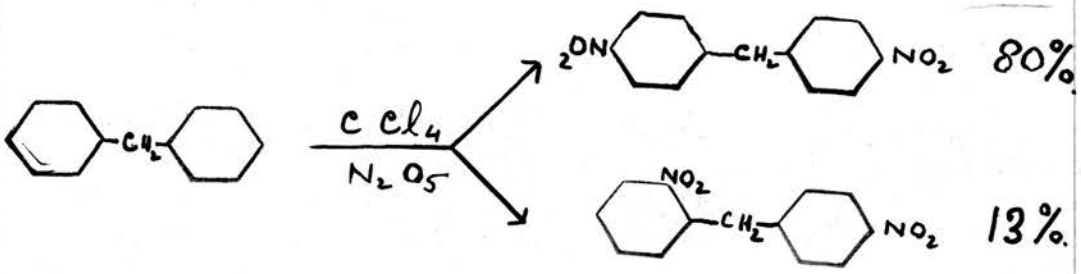


Dinitration of Diphenylmethane in Carbon Tetrachloride at 45°C.

Diphenylmethane (20 g.) was dissolved in carbon tetrachloride (45 c.c.) at 45°C., and nitrogen pentoxide (30 g.) was slowly added. The solid deposited overnight was separated, washed and dried. 4:4'-Dinitro-

diphenylmethane (24 g.) and 2:4'-dinitrodiphenylmethane (3 g.) were isolated, as in previous cases. The carbon tetrachloride filtrate was washed, dried over calcium chloride and evaporated. From the residual oil 1 gramme of 2:4'-dinitrodiphenylmethane was obtained by recrystallisation from alcohol. Total yield 93%.

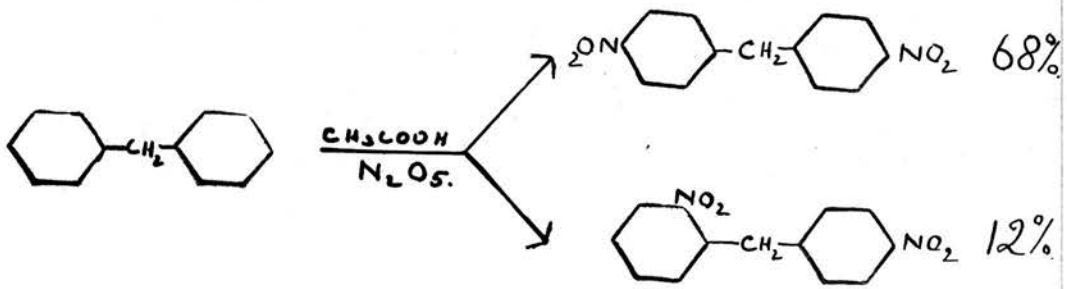
Equation for the reaction:



Dinitration of Diphenylmethane in Acetic Acid at 45°C.

Diphenylmethane (20 g.) dissolved in acetic acid (45 c.c.) was nitrated with nitrogen pentoxide (30 g.) at 45°C. The product was left overnight and poured into water (400 c.c.), the solid was filtered, washed and dried. This solid yielded 21 grammesof 4:4'-dinitrodiphenylmethane and 4 grammes of 2:4'-dinitrodiphenylmethane. Total yield 80%.

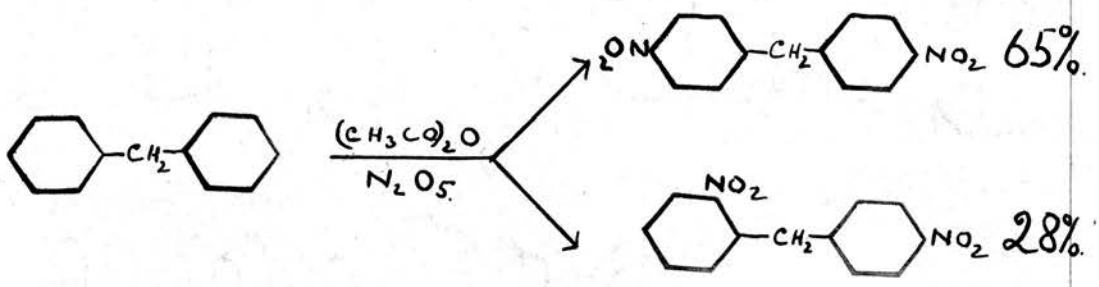
Equation for the reaction:



Dinitration of Diphenylmethane in Acetic Anhydride.

Diphenylmethane (20 g.), dissolved in acetic anhydride (45 c.c.), was nitrated with nitrogen pentoxide (30 g.) at a rate sufficient to maintain the temperature at 45°C. The solution was left overnight, then poured into water (400 c.c.). When all the anhydride had been converted into the acid the solid was filtered, washed and dried. 2:4'Dinitrodiphenylmethane (8·8 g.) and 4:4'-dinitrodiphenylmethane (20 g.) were isolated. Total yield 93%.

Equation for the reaction:



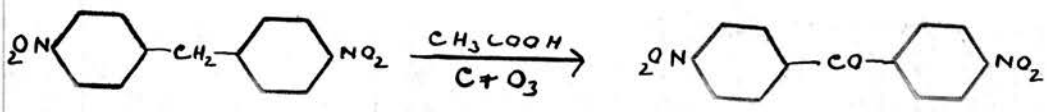
Identification of 4:4'-Dinitrodiphenylmethane by Oxidation to the Benzophenone.

(Staedel, Ann., 1878, 194, 370).

A known sample of 4:4'dinitrodiphenylmethane (1 g.) was dissolved in acetic acid (20 c.c.) in a conical flask, together with chromic acid (1 g.). The solution was refluxed until all the chromic acid had dissolved. Acetic acid (200 c.c.) and chromic acid (3 g.) were then added and the solution refluxed for 20 hours. The solution

was filtered hot and, on cooling, the filtrate deposited 4:4'-dinitrobenzophenone. The crystals were washed with alcohol and recrystallised from acetic acid. Colourless pale yellow prisms of dinitrobenzophenone, m.p. 189°C., were obtained. Similarly the 4:4'-dinitrodiphenylmethane, obtained by nitration of diphenylmethane with nitrogen pentoxide, was oxidised to the same benzophenone, m.p. 189°C. A mixed melting-point determination showed that the two benzophenones were identical, and proved the dinitro compound to be 4:4'-dinitrodiphenylmethane. Yield quantitative.

Equation for the reaction:



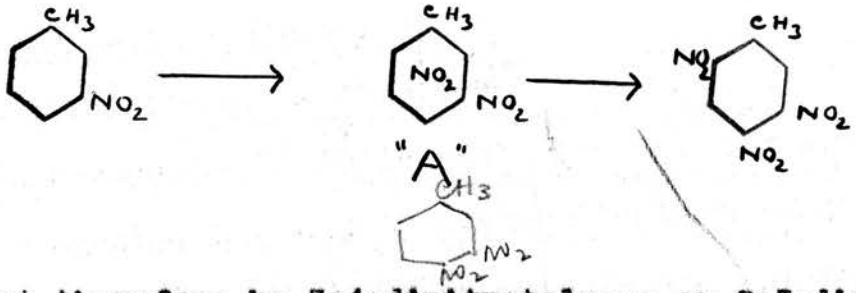
Similarly 2:4'-dinitrodiphenylmethane was identified by oxidation to the 2:4'-benzophenone, m.p. 195°C., in the form of colourless needles.

TABLE of Results for Nitrations of Diphenylmethane.

Solvent		CCl_4	CH_3COOH	CH_3CO / CH_3CO O
Temperature	45°C.	45°C.	45°C.	45°C.
Products of nitration	35·5% 4:4'- 25·5% 2:4'-	80% 4:4'- 13% 2:4'-	68% 4:4' 12% 2:4'	65% 4:4'- 28% 2:4'-
Total Yield	61%	93%	80%	93%

Nitration of m-Nitrotoluene.

Freshly distilled m-nitrotoluene (25 g.) was placed in a flask surrounded by an ice-salt freezing mixture. Nitrogen pentoxide (40 g.), the theoretical quantity for dinitration, was slowly added so that the temperature was maintained at 0 to 5°C. After the addition of the nitrogen pentoxide, the mixture was heated on a brine bath for 6 hours. The mixture was poured into water (300 c.c.) and a heavy yellowish-green oil was deposited, which was extracted with ether, dried over calcium chloride, and evaporated. The residual oil was dissolved in the minimum of boiling alcohol, and on cooling the solution an oil was obtained. Ether was added to redissolve the oil, and on evaporation at room temperature, a yellow solid was deposited. This was separated by filtration, dried, and yielded 10 g. of a compound, m.p. 50°C. Further attempts to obtain crystals from the mother liquor failed, an oil being deposited each time. The solid was recrystallised twice from methyl alcohol. Needles and prisms, m.p. 60°C., were obtained. This nitro compound was further nitrated to give a trinitrotoluene of known structure, namely 3:4:6-trinitrotoluene. We can express graphically these two nitrations, where the compound "A" represents the dinitro- compound, m.p. 60°C.

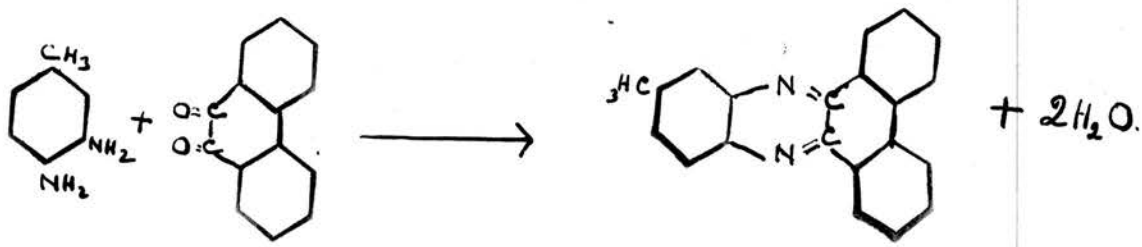


"A" must therefore be 3:4-dinitrotoluene or 2:5-dinitrotoluene; but the melting-point of the latter is 52·5°C., therefore "A" must be 3:4-dinitrotoluene. The constitution of "A" was confirmed by reduction to the corresponding diaminotoluene, which was then condensed with phenanthraquinone to give a known quinoxaline, m.p. 219°C. (lit. 213°C.).

Condensation of3:4-Diaminotoluene with Phenanthraquinone.

5 c.c. of a saturated solution of phenanthraquinone and the diamine, each in hot acetic acid, were mixed. The quinoxaline compound was immediately precipitated. It was separated by filtration, and on recrystallisation from acetic acid yielded pale yellow needles, m.p. 219°C. (lit. 213°C.). This substance gave a loganberry juice colour with concentrated sulphuric acid, characteristic of the quinoxaline family.

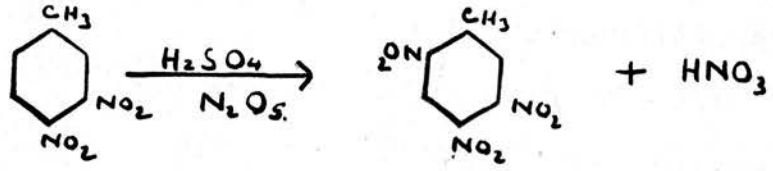
Equation for the reaction:



Nitration of 3:4-dinitrotoluene.

3:4-Dinitrotoluene (1 g.) was dissolved in concentrated sulphuric acid (5 c.c.), and the theoretical quantity of nitrogen pentoxide necessary to introduce a further nitro- group into the molecule was added. The mixture was heated on the water-bath for two hours, and then poured into water. The solid was separated, washed, dried, and recrystallised from alcohol. Pale yellow needles, m.p. 104°C., were obtained. A mixed melting-point showed the substance to be α-trinitrotoluene: i.e., 3:4:6-trinitrotoluene.

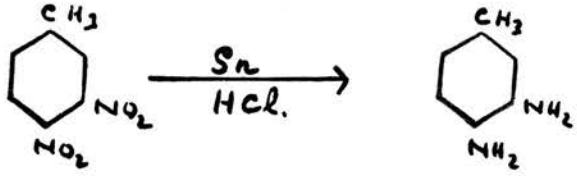
Equation for the reaction:



Reduction of 3:4-Dinitrotoluene to the Diamine.

The method and quantities were the same as for the reduction of 2:4'- and 4:4'-dinitrodiphenyls (page 23). The amine crystallised from ligroin (80° to 100°C.) in glistening yellow plates, m.p. 88°C.

Equation for the reaction:

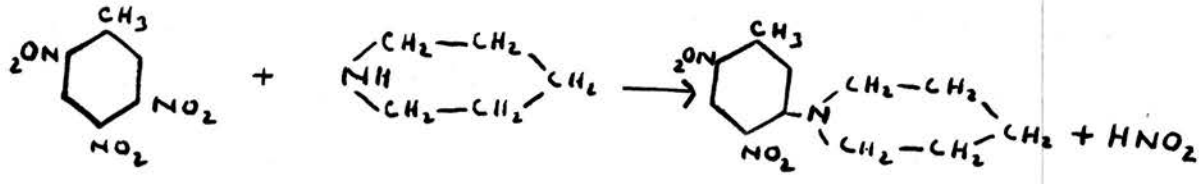


Nitration of m-Nitrotoluene in Concentrated Sulphuric Acid.

m-Nitrotoluene (20 g.) was dissolved in concentrated sulphuric acid (350 c.c.) and the mixture surrounded by iced water. Nitrogen pentoxide (100 g.) representing 6·3 molecules, was slowly added, so that the temperature was maintained at 0°C. to 5°C. The mixture was heated for two hours on the steam-bath before being poured into 500 c.c. water. A pale yellow solid and an oil which rapidly solidified were deposited. The solid w as separated, washed and dried. The theoretical yield, 33·2 g., calculated on the basis of the products being trinitrotoluene was obtained. Hepp (Ann., 1862, 215, 366) records that the solid is a mixture of isomeric trinitrotoluene. The melting point was 80%. Fractional crystallisation from methyl alcohol gave 3:4:6-trinitrotoluene (10 g.), m.p. 104°C. It is well known that 3:4:6-trinitrotoluene condenses with compounds such as piperidine, aniline, methylamine, etc., with the elimination of nitrous acid; fur thermore, these compounds are only sparingly soluble in alcohol. All the filtrates and any solid other than the 10 g. of 3:4:6-trinitrotoluene were poured into water (500 c.c.), and the resulting precipitate separated, washed and dried. Y ield 23 g. 1 g. of this compound, accurately weighed, was dissolved in alcohol (5 c.c.), and 1 g. piperidine added to the hot solution.

The mixture was boiled for one minute and, on cooling, yellow prisms of the condensation compound separated. Two hours were allowed for complete deposition. The crystals were separated and dried in a current of warm air. A correction was made for the solubility of the compound in alcohol (see below) and a control experiment on pure 3:4:6-trinitrotoluene was performed. The result showed that this experiment could be used for an accurate quantitative estimation. From the weight of condensation compound obtained, the weight of pure 3:4:6-trinitrotoluene and the percentage in the mixture were readily calculated. The condensation compound was recrystallised from methyl alcohol and yielded yellow prisms, m.p. 115°C. The alcoholic filtrate containi ng excess piperidine was allowed to evaporate at room temperature until a little solid had accumulated. This was separated and proved to be the condensation compound. The evaporation was then allowed to proceed further in an attempt to establish the constitution of the rest of the original mixture, m.p. 80%. Prisms, m.p. 90 to 110°C., were isolated. The residue is therefore a mixture.

Equation for the reaction:



Solubility of Condensation Compound in Ethyl Alcohol at Room Temperature.

A known weight of compound was shaken with a known volume of ethyl alcohol for two hours. The solid recovered was dried and weighed.

Weight of solid added to 10 c.c. alcohol	0·637 g.
" " " recovered after shaking	0·407 g.
" " " dissolved in 10 c.c. alcohol at room temperature	0·220 g.

The solubility is 0·022 g./c.c. at room temperature.

Control Experiment, using pure 3:4:6-Trinitrotoluene.

Weight of pure trinitrotoluene used	1·2600 g.
Volume of Alcohol	10 c.c.
Weight of Condensation Compound obtained	1·203 g.
Correction for Solubility in Alcohol	0·220 g.
Corrected weight of Condensation Solid	1·423 g.

Amount of 3:4:6-trinitrotoluene in above =

$$1{\cdot}423 \times \frac{227}{265} = 1{\cdot}22.$$

1·22 is in fairly good agreement with 1·26. The difference may be put down to experimental error. The result shows that the method may be used on a quantitative basis with an error of not more than 5%.

Experiments using mixture, m.p. 80°C.

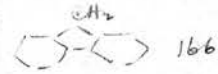
Weight of trinitrotoluene mixture in 15 c.c. alcohol	4·51 g.
Weight of Condensation Compound recovered	2·80 g.
Correction for Solubility	·33 g.
Corrected weight of Compound	3·13 g.

Percentage trinitrotoluene in mixture

$$3{\cdot}13 \times \frac{227}{265} \times \frac{100}{4{\cdot}51} = 61\%$$

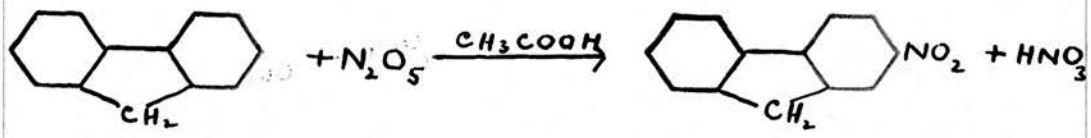
Similar results obtained were 59 and 60%. Thus the mixture contained approximately 60% of 3:4:6-trinitrotoluene, and taking into account the 10 g. 3:4:6-trinitrotoluene already isolated by recrystallisation, the nitration of m-nitrotoluene in concentrated sulphuric acid with a large excess of nitrogen pentoxide leads to 72% of 3:4:6-trinitrotoluene.

Nitration of Fluorene in acetic acid at 45°C.



Fluorene (20 g.) was dissolved in acetic acid (200 c.c.) at 45°C. Nitrogen pentoxide (13 g.), the theoretical quantity for mononitration, was added. The temperature was maintained at 45°C. by external cooling during the addition of nitrogen pentoxide, and then raised to 80°C. for one hour. The mixture was left overnight at room temperature. The yellow solid which had been deposited was separated, washed with water, and recrystallised from alcohol. 2-Nitrofluorene (24 g.), m.p. 154°C., was obtained: i.e., 94%.

Equation for the reaction:



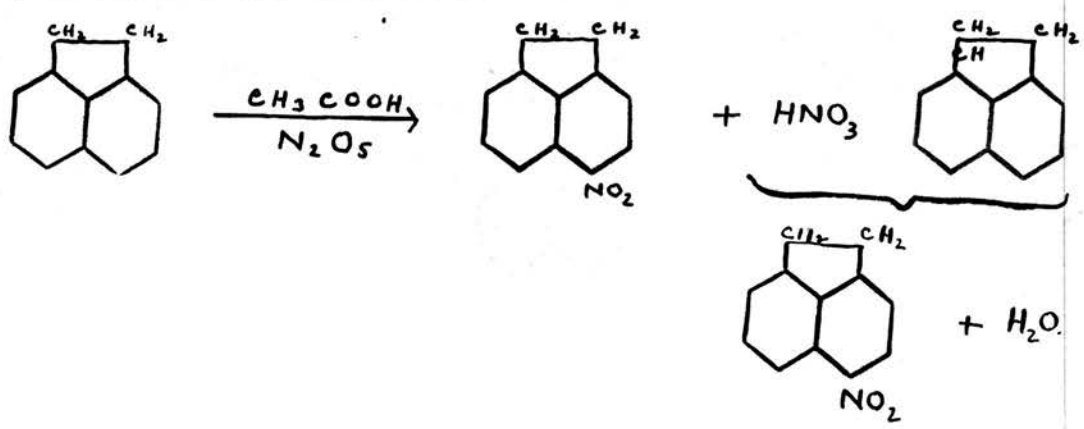
1574

Nitration of Acenaphthene in Acetic Acid at 25°C.

Morgan (J. Soc. Chem. Ind., 1930, 49, 413 T.)

Acenaphthene (20 g.) was dissolved in boiling acetic acid (200 c.c.) and the solution rapidly cooled to 25°C. The greater part of the acenaphthene was deposited as a fine crystalline mass which could be readily nitrated. Nitrogen pentoxide (9 g.), i.e., half the amount theoretically required for mononitration, was slowly added to the well-stirred mixture, the temperature being maintained at 25°C. by external cooling. The yellow crystalline mass deposited overnight was separated, washed and dried. On recrystallisation from alcohol, 4-nitroacenaphthene, m.p. 106°C., was obtained. Yield 33 g., i.e., 99%. Thus the nitric acid liberated had effected nitration.

Equation for the reaction:

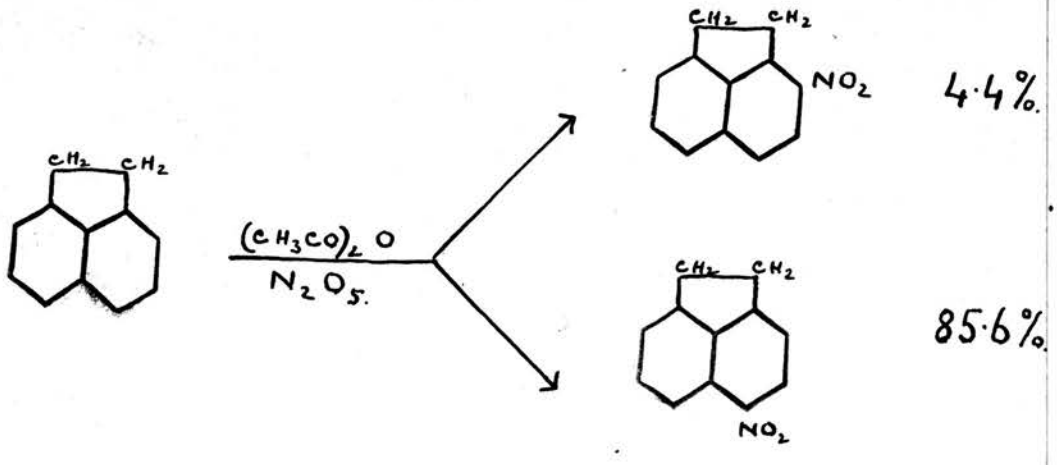


Nitration of Acenaphthene in Carbon Tetrachloride at 25°C.

The experiment was repeated with carbon tetrachloride as solvent. A quantitative yield of 4-nitroacenaphthene showed that the nitric acid liberated had effected nitration.

Nitration of Acenaphthene in Acetic Anhydride.

Acenaphthene (20 g.) was dissolved in hot acetic anhydride (250 c.c.). The solution was rapidly cooled to 10°C., and nitrogen pentoxide (9 g.) was slowly added to this well-stirred suspension at a rate such that the maximum temperature of the solution was 16°C. The solution was left overnight. The solution was cooled to 13°C. and the solid which separated was fractionally crystallised from alcohol, yielding 1·2 g. of yellow needles, m.p. 151°C., i.e., 2-nitroacenaphthene. The mother liquor was poured into water (1.L.). The precipitate was separated, dried, and recrystallised from alcohol, 4-nitroacenaphthene (23 g.), m.p. 106°C. being obtained. Total yield, 90%.



Nitration of Acenaphthene in Acetic Acid at 45°C.

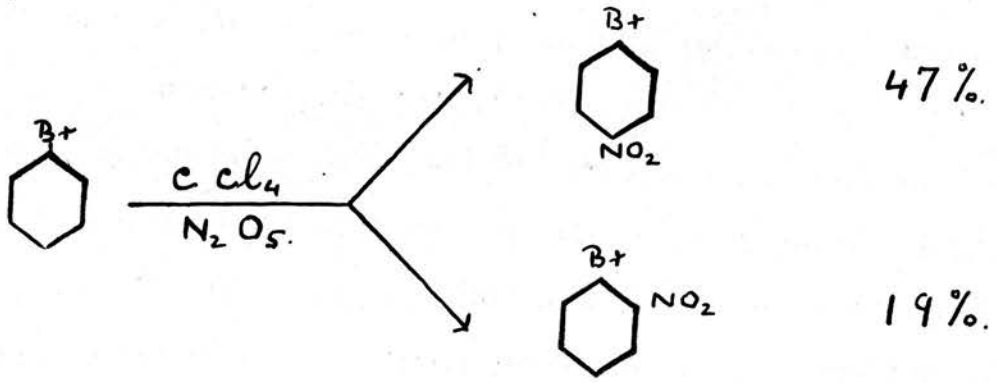
With the amount of nitrogen pentoxide theoretically required for mononitration, i.e. 14 g., a mixture of mono- and di-nitrocompounds was obtained. The melting point of this mixture was 120°C. Fractional recrystallisations from ethyl alcohol and methyl alcohol were unsuccessful, as also were attempts to separate the compounds by sublimation.

Similar results with (1) acetic anhydride and (2) carbon tetrachloride as solvent were obtained.

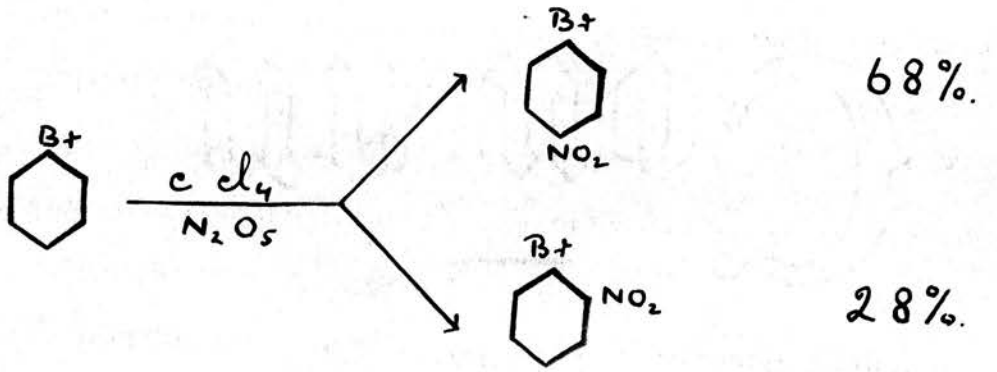
Nitration of bromobenzene in Carbon Tetrachloride at 45°C.

Nitrogen pentoxide (13·8 g.), the theoretical amount for mononitration, was added to bromobenzene (20 g.) dissolved in carbon tetrachloride (45 c.c.), the temperature being maintained at 45°C. by external cooling. The mixture was poured into water (300 c.c.), the solid and carbon tetrachloride layers were extracted with ether, the ethereal extract dried over calcium chloride, and the ether evaporated. The residual solid was dissolved in the minimum of hot 50% alcohol. The solution was cooled to room temperature and the crystals were separated and dried. para-Bromonitrobenzene (12 g.) in the form of prisms, m.p. 122°C., was isolated. The alcohol was allowed to evaporate from the filtrate at room temperature, yielding yellow

needles, m.p. 40°C., i.e. ortho-nitrobromobenzene; yield 5 g.

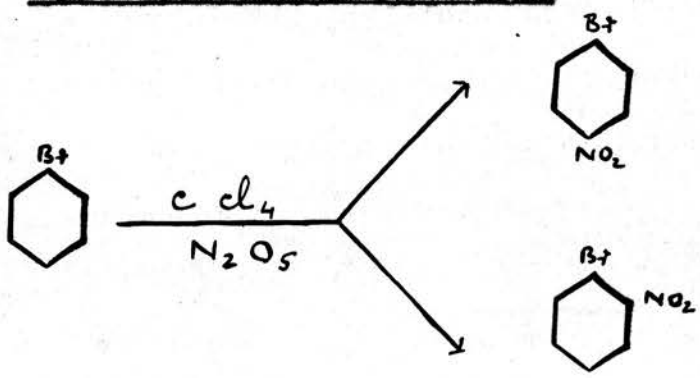


The nitration was repeated at 5°C.., when para-bromonitrotoluene (17·2 g.) and ortho-bromonitrobenzene (7·2 g.) were obtained. Yield, 96%. Hence, a low temperature of reaction raises the yield.



The nitration was repeated at 25°C., using two molecular proportions of nitrogen pentoxide. para-Nitrobromobenzene (21·5 g.) and ortho-nitrobromobenzene (4·5 g.) were obtained. Yield quantitative. No dinitro compound was detected. Haines and Adkins (J. Amer. Chem. Soc., 1925, 47, 1419) claim to have obtained a quantitative yield of p-bromonitrobenzene at 0°C.

Equations for the reaction:



82·5%

17·5%.

Bromobenzene (20 g.) was nitrated with varying amounts of nitrogen pentoxide at different temperatures and in different solvents. The results obtained are tabulated overleaf.

Solvent	Temperature	Moles of N_2O_5	Yield of p-	Yield of o-	Total Yield
45 c.c. CCl_4	45°C.	1 mole	47%	19%	66%
45 c.c. CCl_4	5°C.	1 "	68%	28%	96%
45 c.c. CCl_4	25°C.	2 "	82·5%	17·5%	100%
45 c.c. CH_3COOH	10°C.	1 "	42·5%	3·9%	46·4%
45 c.c. CH_3COOH	45°C.	1 "	22·2%	7·2%	29·4%
45 c.c. CH_3COOH	10°C.	2 "	70%	17·6%	87·6%
45 c.c. $(CH_3CO)_2O$	10°C.	1 "	33%	8·3%	41·3%
45 c.c. H_2SO_4	10°C.	0·5 "	38%	-	38%
45 c.c. H_2SO_4	10°C.	1 "	82%	13%	95%
No Solvent	45°C.	1 "	90%	(4-bromo-1:3-dinitro) 4%	98%

The effect of a catalyst on the reaction was also investigated.

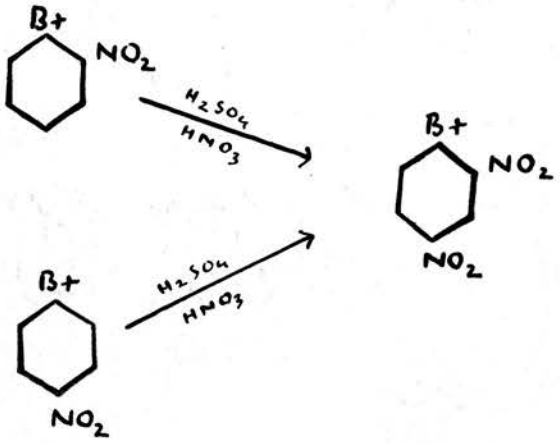
<u>With mercuric nitrate (1 g.) as catalyst:</u>					
45 c.c. CCl_4	5°C.	1 mole	62%	33%	95%
<u>With mercury (1 g.) as catalyst:</u>					
45 c.c. CCl_4	5°C.	1 mole	65%	27%	92%
<u>Nitration of Chlorobenzene (20 g.) without catalyst:</u>					
45 c.c. CCl_4	5°C.	1 mole	42%	-	42%
<u>Nitration of Iodobenzene (20 g.) without catalyst:</u>					
45 c.c. CCl_4	5°C.	1 mole	69%	12%	81%

The Identification of ortho- and para-Bromonitrobenzene.

o-Nitrobromobenzene (10 g.) dissolved in 30 c.c. H_2SO_4 (d 1·83) was nitrated with 30 c.c. fuming nitric acid. The solution was boiled for 10 minutes, cooled, poured into water (200 c.c.) and filtered. The solid was recrystallised from ethyl alcohol. Pale yellow prisms, m.p. 75°C., i.e. 4-br omo-1;3-dinitrobenzene, were formed.

Similarly 4-bromo-1;3-dinitrobenzene was obtained by the nitration of p-bromonitrobenzene.

Equation for the reaction:



Nitration of Aniline in Carbon Tetrachloride at 0°C.

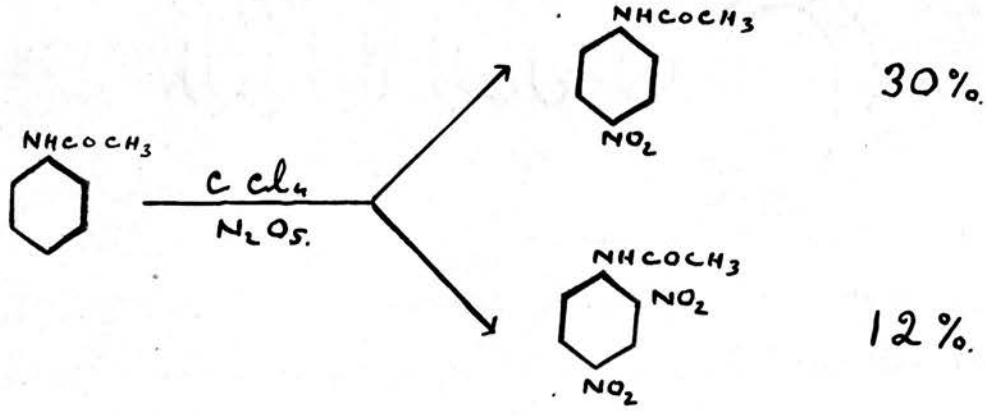
An attempt was made to nitrate aniline, dissolved in carbon tetrachloride at 0°C. with nitrogen pentoxide. The reaction, however, was too vigorous and the product charred.

Nitration of Acetanilide in Carbon Tetrachloride at 10°C.

Nitrogen pentoxide (16 g.), the theoretical

quantity for dinitration, was added in portions to acetanilide (10 g.) dissolved in carbon tetrachloride (25 c.c.) at 10°C. The product was kept overnight and then poured into water. The carbon tetrachloride layer was washed free from nitric acid, separated, dried over calcium chloride, and finally evaporated. The residual solid was fractionally recrystallised from 50% alcohol. p-Nitracetanilide (4 g.), m.p. 206°C., and 2:4-dinitracetanilide (2 g.), m.p. 120°C., were isolated, the latter being the less soluble. The constitution of the latter was confirmed by hydrolysis with 50% sulphuric acid to 2:4-dinitroaniline, m.p.176°C. Total yield, 42%.

Equation for the reaction:



Unchanged acetanilide (mixed melting point) was isolated when one molecular proportion of nitrogen pentoxide was used.

Nitration of Desoxybenzoin.

No nitration occurred with carbon tetrachloride, acetic acid, or sulphuric acid as solvent, and either 1 or 2 molecular proportions of nitrogen pentoxide. Nitration without a solvent gave a low yield of para-nitrodesoxybenzoin, m.p. 145°C., which was separated from unchanged desoxybenzoin by repeated recrystallisations from petrol ether and benzene in the ratio of 1:1.

Nitration of Benzoin Acid in Acetic Acid at 20°C.

No nitration occurred; confirmed by a mixed melting point determination.

Nitration of Benzaldehyde in Acetic Acid at 20°C.

No nitration occurred. Unchanged compound was isolated (dinitrophenylhydrazine, m.p. 230°C.).

Preparation of pure m-Dinitrobenzene.

cf. Pounder and Masson (J. Chem. Soc., 1934, 1359 T.)

m-Dinitrobenzene was prepared by a two-stage nitration of pure thiophene-free A.R. benzene with sulphuric and nitric acids. The nitrobenzene was purified by distillation before being further nitrated. The dinitrobenzene was recrystallised from alcohol and dried. It was refluxed with a solution of sodium methylate in anhydrous methyl alcohol for two hours to remove isomers and traces of trinitrobenzene as phenoxides. The dinitrobenzene was removed from the

cold solution, dried, and recrystallised three times from alcohol. The long cream-coloured needles were dried on a plate at 60°C. for 2 hours, and finally in a vacuum desiccator overnight. A melting-point apparatus similar to that used by Pounder and Masson (loc. cit.) was set up, and the figures obtained were compared with the figures obtained by the above authors. Dinitrobenzene (·2 g.) was ground up and introduced into a tube of cross-section (2 mm.) and about 9 cm. long, sealed at one end. The tube was clamped to a standard thermometer and held in place in a bath of glycerine which was well stirred. The flame from the bunsen could be adjusted so that the temperature of the bath rose by 0·1°C. per 2 min. The bath was heated quickly to about 10°C. below the melting point of the compound, and then very slowly. The solid wasfrequently stirred by a thin glass rod. The temperature at which the last crystals disappeared was taken as the melting point. By this method the melting point of m-dinitrobenzene was found to be 90·0°C. (cf. 90·2°C. recorded by Pounder and Masson). The apparatus modified so as to include an air chamber between the glycerine and the melting point tube was not so satisfactory. The melting point of m-dinitrobenzene by this means was 89 - 90·5°C. Para-dinitrobenzene was purified by sublimation and a mixture of this compound and the meta compound was made up, having the composition 90·2% meta. The melting point of this mixture was 83·8°C. (cf. 83·9% for a

similar mixture obtained by Pounder and Masson). The apparatus and method, therefore, were found to be satisfactory.

Thermal analysis of Dinitrobenzenes.

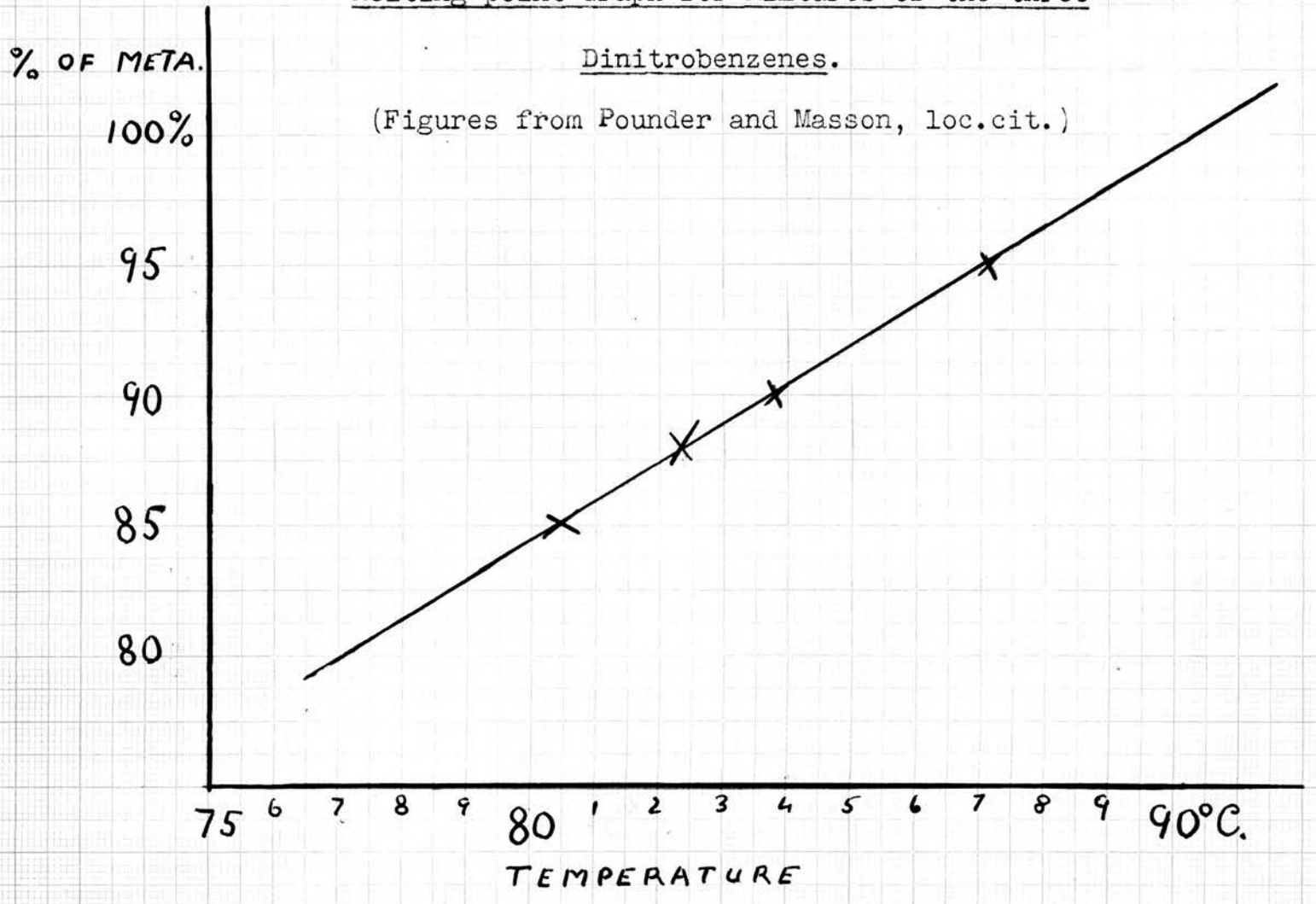
Nitrogen pentoxide (9 g.), the theoretical quantity for mononitration, was slowly added to thiophene-free nitrobenzene (10 g.). A vigorous reaction resulted and the temperature was maintained at 45°C. by external cooling. The solution was left overnight and poured into water (100 c.c.). The solid was melted under water (100 c.c.) three times, and when liquid, was well shaken. The solution was cooled to room temperature and filtered. Finally it was ground and dried on a plate at 60°C. for 3 hours, and then overnight in a vacuum desiccator. The melting point of a sample was 88·4°C. From the results obtained by Pounder and Masson (loc. cit.) a melting point curve for mixtures of the dinitrobenzenes was plotted. From the above curve a melting point of 88·4°C. corresponded to 97% metadinitrobenzene.

Dinitration of thiophene-free benzene.

Thiophene-free (A.R.) benzene was dinitrated with nitrogen pentoxide (28 g.), i.e. 2 molecular proportions, at 45°C. The solid obtained received the same treatment as above. The melting point was 86·1°C., representing 93·5°C meta

Melting point Graph for Mixtures of the three Dinitrobenzenes.

(Figures from Pounder and Masson, loc.cit.)



Nitration of Nitrobenzene in (1) Acetic Acid
(2) Acetic Anhydride
(3) Carbon Tetrachloride

Nitrogen pentoxide (18 g.) was added to nitrobenzene (10 g.) dissolved in 25 c.c. of solvent. In each case no nitration occurred and unchanged nitrobenzene, b.p. 207°C., was isolated.

Nitrobenzene (10 g.) was dissolved in varying amounts of sulphuric acid (d 1·83) and nitrated with varying amounts of nitrogen pentoxide at different temperatures. The solids obtained were treated as before, and the melting points determined.

The results are tabulated overleaf.

Volume of H_2SO_4	Moles of H_2SO_4	Temperature	Moles of N_2O_5	M.p. of mixture	% meta from graph	Yield	Expt. No.
20 c.c.	·37	20°C.	1 mole	83·1°C.	89·0% m	13·2 g.	A
20 c.c.	·37	45°C.	" "	82·1°C.	87·7% m	13·0 g.	B
20 c.c.	·37	80°C.	" "	80·8°C.	85·75% m	13·0 g.	C
40 c.c.	·75	45°C.	" "	83·3°C.	89·5% m	12·9 g.	D
55 c.c.	1·0	45°C.	" "	83·0°C.	89·0% m	13·3 g.	E
70 c.c.	1·3	45°C.	" "	83·0°C.	89·0% m	13·3 g.	F
90 c.c.	1·7	45°C.	" "	84·2°C.	90·7% m	13·1 g.	G
100 c.c.	1·86	45°C.	" "	85·1°C.	92·0% m	13·0 g.	H
20 c.c.	·35	45°C	·5 "	Too oily to treat.		HNO_3 did not nitrate	
None	-	45°C.	1 "	88·4	97·0% m	13·3 g.	K

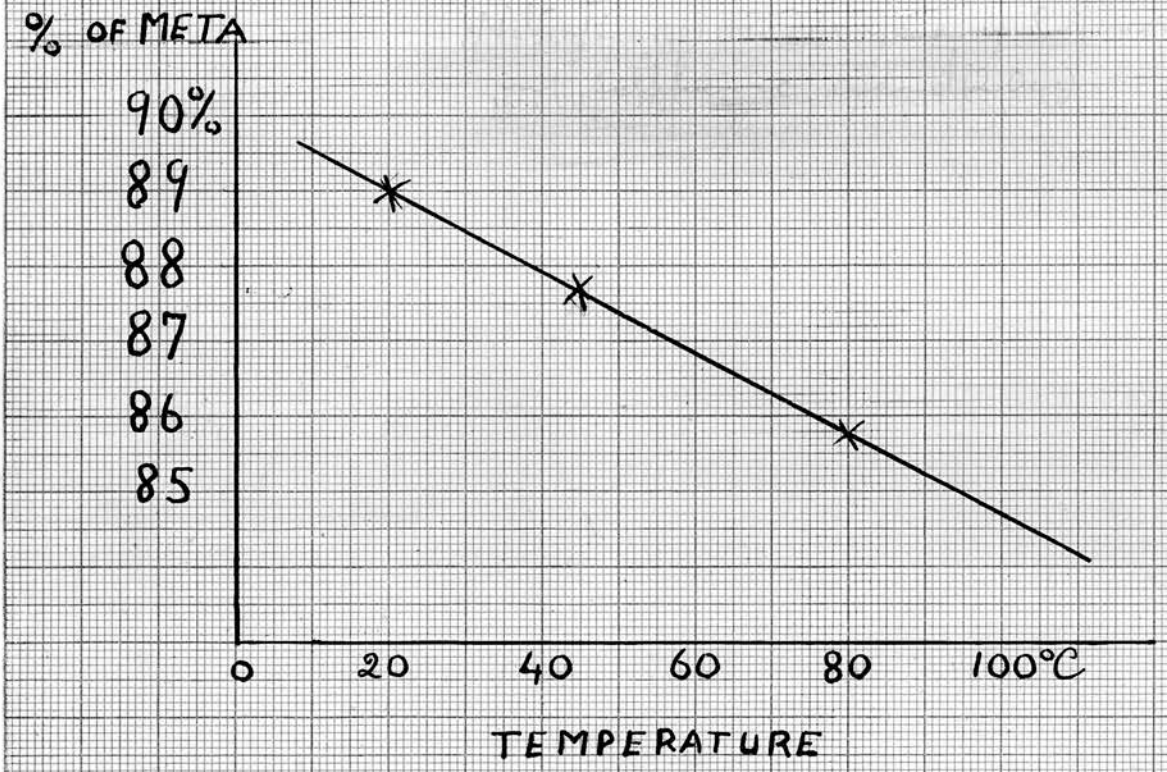
In the case of A, B and C, the % meta obtained was plotted against the temperature. A straight line relationship was found to exist (See Graph). In the case of B, D, E, F, G, H and K, the % meta obtained was plotted against the amount of sulphuric acid used. From the resulting curve, it is evident that the sulphuric acid is not merely a solvent, but that it influenced the percentage of meta formed.

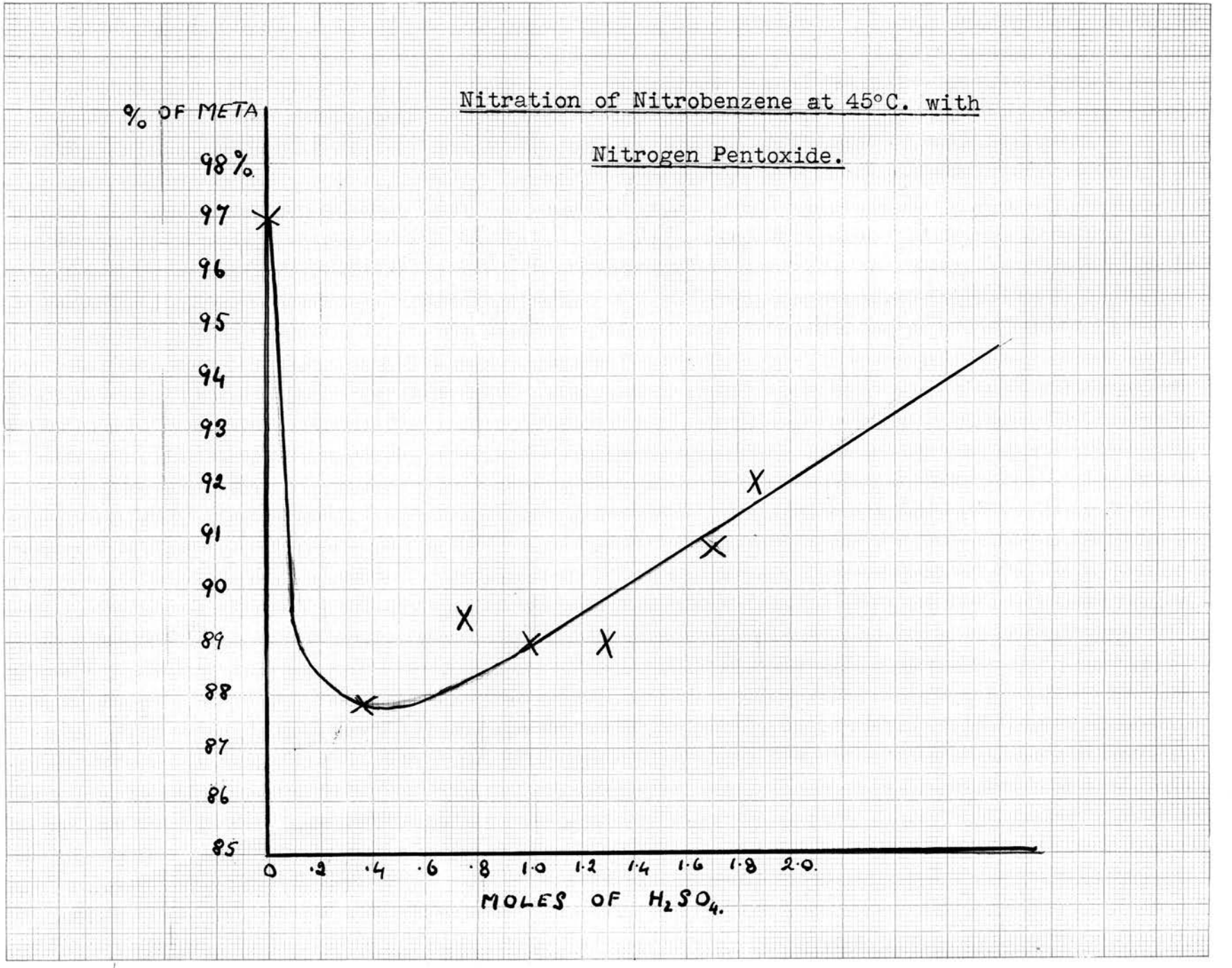
Thermal analysis of the Nitrodiphenyls.

Melting point curve for mixtures of 2-Nitro and 4-nitro diphenyl.

Nitration of Nitrobenzene in Sulphuric Acid (20 c.c.)

with Nitrogen Pentoxide.

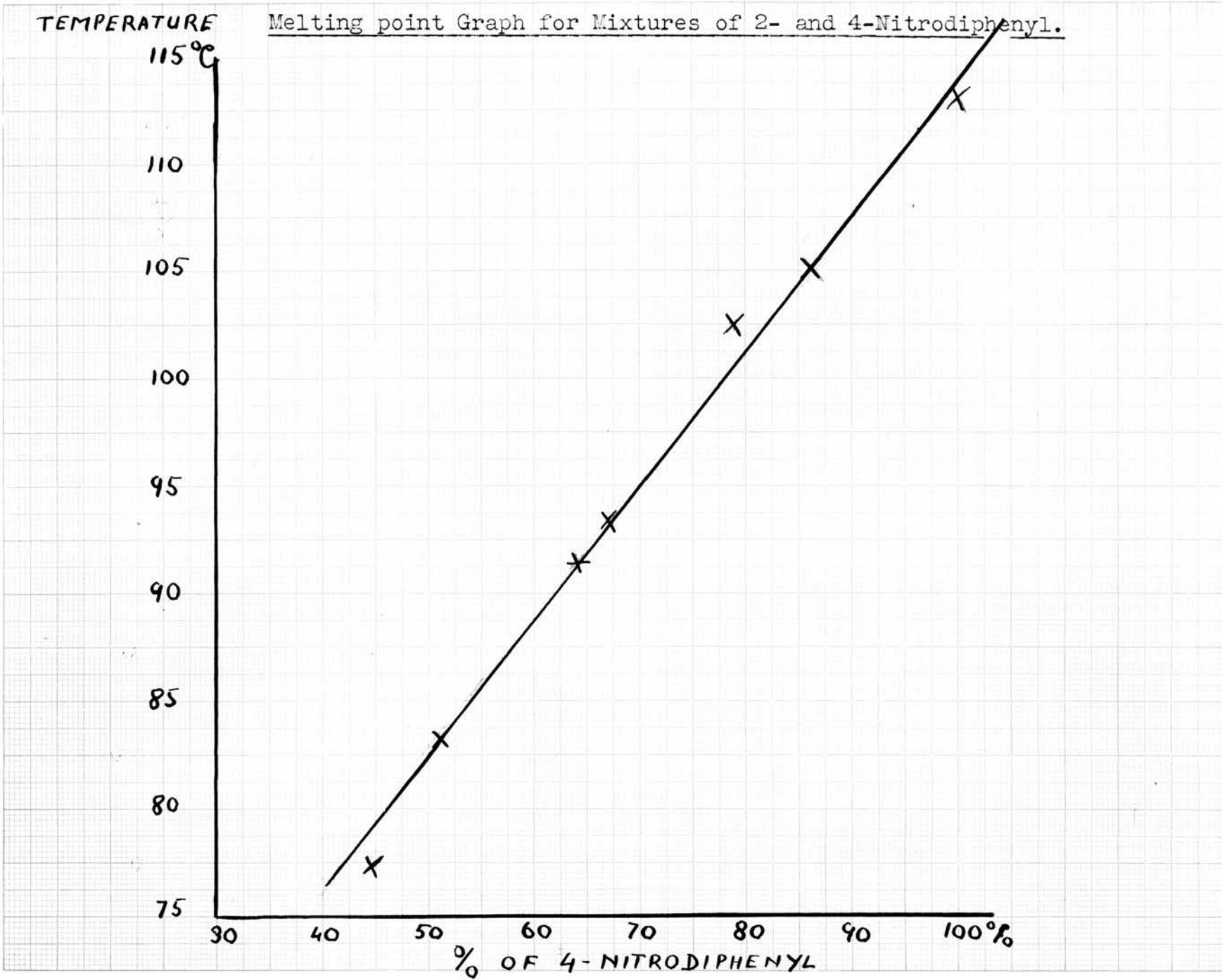



Nitration of Nitrobenzene at 45°C. with
Nitrogen Pentoxide.
% OF META
98%
97
96
95
94
93
92
91
90
89
88
87
86
85
0
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0.
MOLES OF H_2SO_4.

2-Nitrodiphenyl was purified by distillation at 35 mm. The main bulk distilled between 202° and 205° as a yellow oil which readily solidifed on "seeding". This solid was recrystallised from the minimum quantity of boiling methyl alcohol, then filtered, ground and dried in a vacuum desiccator over phosphorous pentoxide. 4-Nitrodiphenyl was recrystallised from methyl alcohol, then filtered, dried on a hot plate at 60°C. for 3 hours, and finally in a vacuum desiccator overnight, m.p.113·5°C. The melting point of mixtures, in which the percentage of 4-nitrodiphenyl varied between 40% and 100%, was determined as follows:- The mixture, contained in a weighing bottle, was heated over a small flame until liquid, when, after thorough mixing, it was cooled, ground and dried in a desiccator. The melting point was determined as before. Mixtures containing a high percentage of 2-nitrodiphenyl were oils, with the result that the complete curve was not obtained. However it was known that the percentage of the 2-isomer obtained on nitration did not exceed 40%. The percentage composition and the corresponding melting points are tabulated below.

Percentage of 4-nitrodiphenyl	Melting-point
100%	113·5°C.
85·9%	105·7°C.
79·0%	102·7°C.
66·8%	93·7°C.
64·1%	91·5°C.
51·2%	83·2°C.
44·8%	77·3°C.

Diphenyl was nitrated with nitrogen pentoxide in carbon


TEMPERATURE
Melting point Graph for Mixtures of 2- and 4-Nitrodiphenyl.
115°C
110
105
100
95
90
85
80
75
30
40
50
60
70
80
90
100%
% OF 4-NITRODIPHENYL

tetrachloride, acetic acid, acetic anhydride or sulphuric acid. In each case the solid isolated was oily and contained traces of dinitrodiphenyl rendering thermal analysis impossible.

Melting-point Curve for mixtures of 2- and 4-nitroacenaphthene.

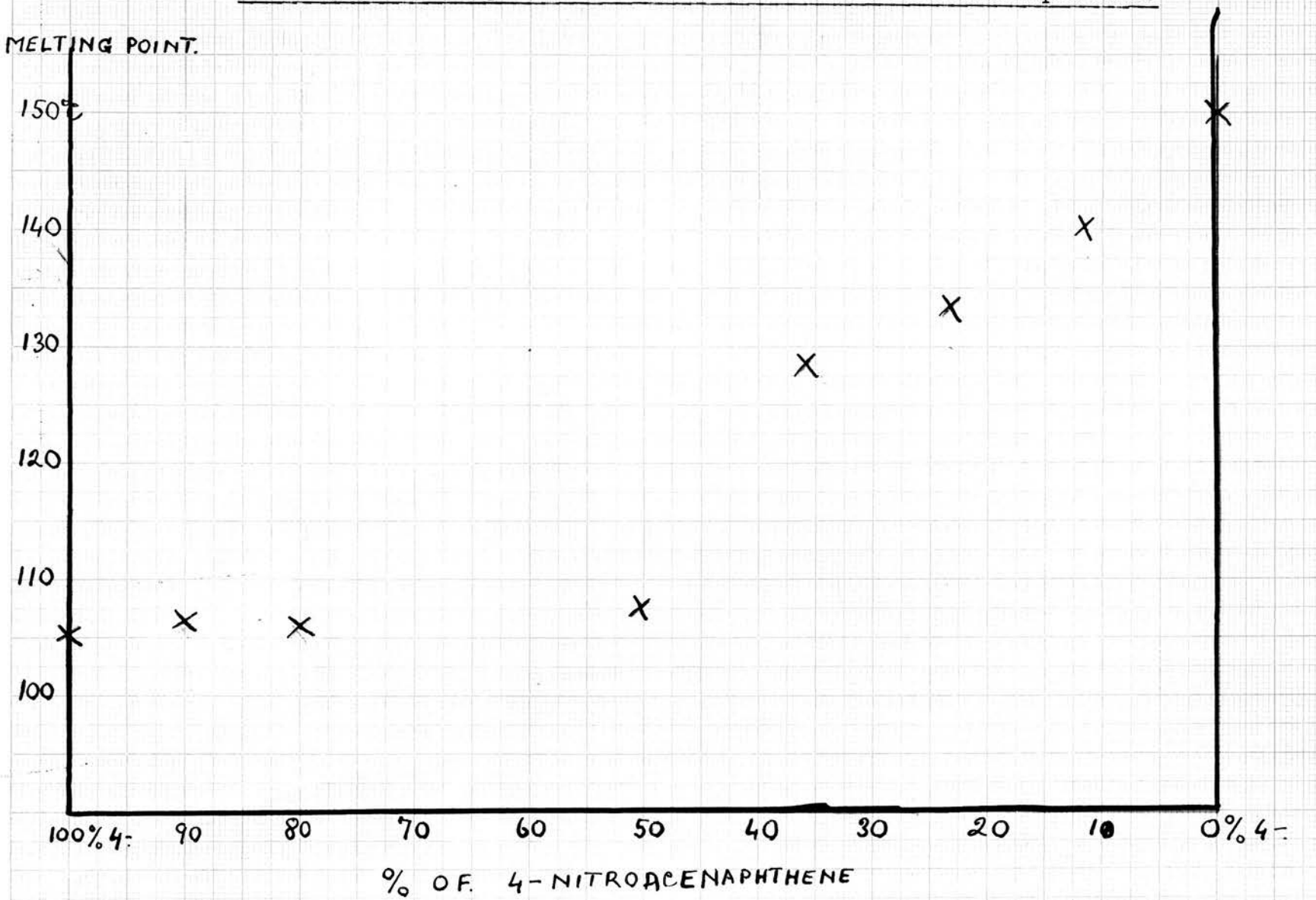
4-Nitroacenaphthene was recrystallised five times from methyl alcohol, dried on a plate at 60°C. for 3 hours, and finally overnight in a vacuum desiccator. The melting point was found to be 105·5°C. Further purification did not alter the melting point. This product was therefore taken as pure 4-nitroacenaphthene. 2-Nitroacenaphthene was prepared by the nitration of acenaphthene with diacetylorthonitric acid by the method of Morgan (J. Soc. Chem. Ind., 1930, 49, 413 T.). The yield was 20%. The pure 2-nitroacenaphthene melted at 149·9°C. Mixtures of these isomers were prepared in the following way:- A watch glass containing weighed quantities of the two isomers was heated over a small flame to melt the mixture. By tilting the watch-glass thorough mixing was obtained. The mixture was allowed to solidify and then finely ground. 0·2 g. of the mixture was used for the melting point determination.

The melting points obtained for mixtures of varying composition are tabulated overleaf:

% of 4-nitroacenaphthene.	m.p. of mixture.
0%	149·9°C.
11·5%	140·3°C.
23·0%	133·5°C.
36·0%	128·6°C.
50·5%	107·5°C.
80·0%	106·2°C.
90·0%	106·5°C.
100·0%	105·6°C.

These results were plotted on a graph; but the usual type of curve was not obtained. The nature of the curve from the points obtained was not apparent. The formation of a molecular compound was assumed to have taken place.

Melting point Graph for Mixtures of 2- and 4-Nitroacenaphthene.



The Trinitration of fluoranthene in acetic acid at 70°C.

Fluoranthene (10 g.) was dissolved in acetic acid (50 c.c.) and nitrogen pentoxide (16 g.) (i.e., three molecular proportions) was added, the temperature being maintained at 70°C. by external cooling. The mixture was allowed to stand for one hour. The solid was separated and recrystallised from concentrated nitric acid, when yellow needles, m.p. 310°C. (d), were obtained. This substance was identical with trinitrofluoranthene which had been analysed (see page 69). Yield, quantitative.

Attempted oxidation of trinitrofluoranthene.

cf. Fittig (Ann., 1880, 200, 1).

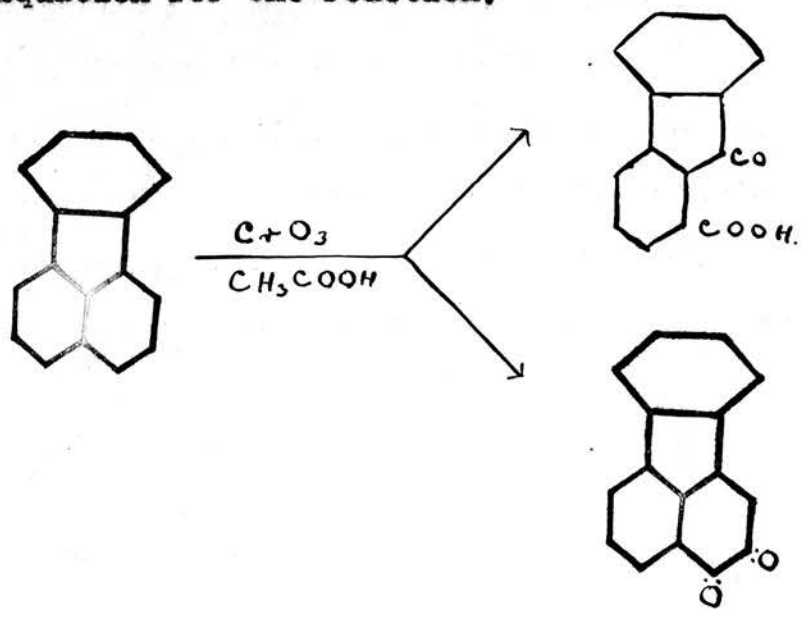
The nitro compound (0·5 g.) was refluxed with a solution of chromic oxide (1 g.) dissolved in acetic acid (15 c.c.) and water (2 c.c.) for one hour. The solution was cooled, poured into water (100 c.c.) and then filtered. The solid obtained was shaken with aqueous sodium carbonate, filtered, and the filtrate acidified with hydrochloric acid, but no solid was deposited. The compound insoluble in the alkali was recrystallised from concentrated nitric acid, when needles, m.p. 310°C., were obtained. These crystals were found to be unchanged trinitrofluoranthene by a mixed melting point determination. No oxidation occurred with the following reagents.

1. A large excess of chromic oxide in acetic acid.
2. Potassium dichromate in sulphuric acid.
3. Nitric acid (D. 1·2 and 1·4) in a sealed tube for 20 hours at 200°C.
4. Sodium peroxide as used by Wills (Ber., 1895, 28, 374) to oxidise 1:4:5-trinitronaphthalene.
5. Iodic acid according to the method of Williams (J.A.C.S., 1921, 43, 1911).

Oxidation of fluoranthene.

The method of Fittig (loc. cit.) was repeated with fluoranthene. Fluorenone-1-carboxylic acid, m.p. 188°C., was isolated from the sodium carbonate solution on acidification. The residue, insoluble in sodium carbonate, was washed and dried, m.p. 102°C., i.e., Fittig's complex formed by the union of fluoranthene and fluoranthenequinone. A micro-sublimation of this solid was carried out at 150°C. Red needles of fluoranthenequinone (m.p. 200°C.) were obtained. Yields poor.

Equation for the reaction:



Improved method, Fieser & Seligman, J.A.C.S., 1935, 57, 2174

Cf. v. Braun & Anton, Ber., 1929, 62, 151.

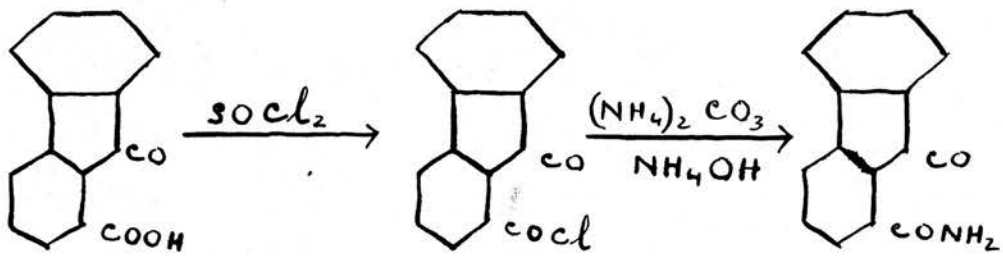
Oxidation also took place with acid dichromate but not with acid or alkaline permanganate or iodic acid.

Preparation of fluorenone-1-carboxylic acid amide.

Goldschmidt (Monats., 1902, 23, 890).

Fluorenone-1-carboxylic acid (3 g.) and thionyl chloride (5 g.) were refluxed on a water-bath for half-an-hour. The excess thionyl chloride was removed by a water-pump. The residual solid was recrystallised from benzene. Yellow needles of fluorenone-1-carboxylic acid chloride were obtained, m.p. 140°C. (lit., 140°C.). The chloride was ground with ammonium carbonate and concentrated ammonia and heated on the water-bath for 15 minutes. The solid was poured into water, and well mixed and filtered. The solid was recrystallised from alcohol, yielding greenish-yellow needles of fluorenone-1-carboxylic acid amide, mp. 230°C. (lit. 230°C.).

Equation for the reaction:



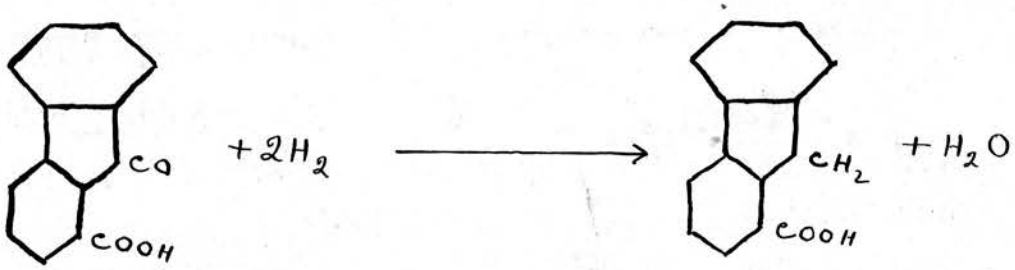
Reduction of fluorenone-1-carboxylic acid.

Fittig (loc. cit.)

Finely-ground fluorenone-1-carboxylic acid (4 g.) was suspended in water (70 c.c.). 4% sodium amalgam (170 g.)

was added in portions, with frequent shaking, and dilute hydrochloric acid was added at intervals to neutralise partly the sodium hydroxide formed, the solution being kept alkaline throughout. The liquid was placed on the water-bath for 2 hours. It was cooled, and filtered through a sintered glass filter. On acidifying the filtrate, the fluorene acid was precipitated. It sublimed at 200°C. to give white needles, m.p. 248°C. (lit. 245°C.).

Equation for the reaction:



Attempted reduction of trinitrofluoranthene.

cf. Aguiar Lautemann (Bull Soc. Chim., 1865, 3, 263).

Trinitrofluoranthene (1 g.) was suspended in concentrated hydrochloric acid (25 c.c.) and alcohol (2 c.c.). Tin was added and the solution was refluxed for 2 hours. The hot solution was filtered. The solid obtained was found to be unchanged trinitrofluoranthene, m.p. 310°C. (mixed melting point 310°C.). The filtrate was cooled but no solid was deposited.

No reduction of the trinitrofluoranthene was obtained when stannous chloride in acetic acid saturated

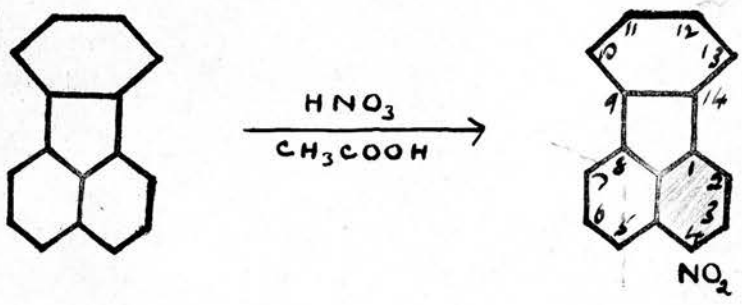
with hydrochloric acid gas, or quinoline and sulphuretted hydrogen were used.

The Mononitration of fluoranthene in acetic acid at 30°C. (cf. von Braun & Irmisch, Annalen, 1931, 488, 173) method was modified as follows-

Fluoranthene (1 g.) was dissolved in the minimum quantity of acetic acid at 30°C., i.e. 50 c.c. To the mechanically-stirred solution nitric acid (5 c.c.) D (1·51) was added drop by drop. The solution was stirred for 2 hours after the addition of the nitric acid, and left overnight at room temperature. The solid which had been deposited was separated; m.p. 148°C. approx. The solid was recrystallised from ethyl acetate. Yellow needles, m.p. 159°C., were obtained, i.e. 4-nitrofluoranthene (lit. 159-160°C.). Yield, 60%. v. Braun, only 20%.

gerty's results not confirmed. 17/3/43. a4R.

Equation for the reaction:



Bromination of nitrofluoranthene.

No bromination occurred when carbon disulphide was used as solvent, even after 24 hours refluxing. Nitro-

fluoranthene was added in small portions to bromine. The mixture was heated on the steam-bath to remove excess bromine, and the residual solid was washed with dilute sodium hydroxide and then with water. Bromine was found to be present in the solid, which, after successive recrystallisations from acetic acid, melted at 250-53°C. This compound was found to be tribromo-nitrofluoranthene, as a result of a bromine analysis. Found: 51·6% bromine; $C_{16}H_6Br_3NO_2$ requires 49·7% bromine.

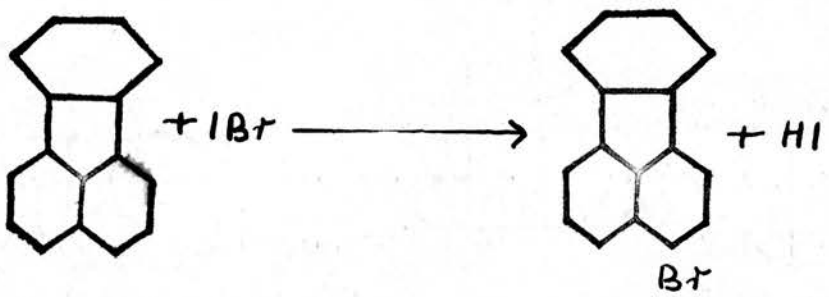
cf. v Braun & Irmg (Annalen, 1931, 488, 115) Our method preferable.

Bromination of fluoranthene using iodine bromide.

cf. Walter Militzer (J. Am. Chem. Soc., 1938, 60, 256)

Fluoranthene (5 g.) was dissolved in carbon tetrachloride (30 c.c.) at 50°C. Three molecular proportions of iodine bromide in carbon tetrachloride at 50°C., made by adding the required quantity of bromine to a carbon tetrachloride solution of iodine, were added in three portions at intervals of 10 minutes. The mixture was maintained at 50-60°C., until the evolution of hydrobromic acid had ceased. The mixture was cooled and filtered. The solid obtained dissolved in sodium thiosulphate and was therefore iodine. The filtrate was shaken with water to remove hydrobromic acid, then with sodium hydroxide to remove iodine, and finally with water to remove alkali. The carbon tetrachloride layer was separated, dried over calcium chloride, and evaporated. The residual solid (6 g.)

m.p. 85-95°C., was impure monobromofluoranthene. It was converted to the picrate which, when recrystallised from alcohol, yielded yellow needles, m.p. 130-1°C.(8 g.) The picrate was dissolved in chloroform and decomposed with alkali. Sodium picrate was separated by filtration. The chloroform layer was washed, dried and evaporated. The residual solid (4·5 g.), m.p. 102-3°C. (lit. 102°C.) was 4-bromofluoranthene. Total yield, 70%. Equation for the reaction:



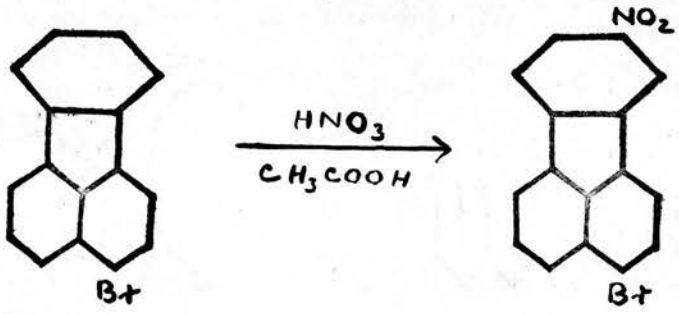
$$IBr + HI \longrightarrow I_2 + HBr$$

Nitration of monobromofluoranthene.

4-Bromofluoranthene (1 g.) was dissolved in acetic acid (100 c.c.) at 30°C. Fuming nitric acid (5 c.c.) was added through a dropping funnel to the well-stirred solution at a rate such that the temperature was maintained at 30°C. The solution was stirred for 1 hour after the addition of the acid at room temperature. The solid was separated, and on recrystallisation from acetic acid, yellow needles, m.p. 237-8°C., were obtained.

method repeated (3 mins 1 min) Heating at 50° necessary.

As a result of analysis for bromine and nitrogen, the compound was shown to be bromonitrofluoranthene.
Found: 24·44% bromine; 4·7% nitrogen.
$C_{16}H_8BrNO_2$ requires 24·50% bromine; 4·3% nitrogen.



An attempt was made to nitrate 4-bromofluoranthene with fuming nitric acid, but the product isolated, when treated with sodium carbonate solution, darkened and became viscous, showing that extensive oxidation had occurred. The compound could not be purified by recrystallisation or by boiling with charcoal.

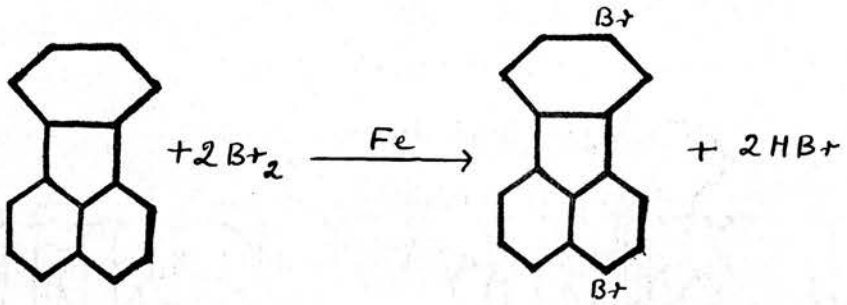
Dibromination of fluoranthene.

von Braun (Ann., 1931, 488, 115).

Fluoranthene (20 g.) was dissolved in carbon disulphide (100 c.c.) and the solution was cooled to 5°C. Iron filings (0·5 g.)were added as catalyst. Bromine (16 g.), representing two molecular proportions, was added through a dropping funnel to the mechanically-stirred solution. When evolution of hydrobromic acid gas had ceased, the solid which has separated was removed by filtration, and the filtrate, consisting of

32.

a mixture of mono- and di-bromofluoranthene and unchanged fluoranthene, was discarded. The solid was triturated with alcohol to remove any bromine, and the mixture was decanted from the catalyst. The solid was separated by filtration and purified by boiling with alcohol. The solid readily sublimed at 190°C. to give yellowish-green prisms, m.p. 205°C. This method of purification has not previously been recorded.
Yield 20 g., i.e. 60%.
Equation for the reaction:



Oxidation of Dibromofluoranthene.

The method was the same as that used in the oxidation of fluoranthene (p. 54). The acid obtained from the sodium carbonate extract was recrystallised from alcohol and melted over a range (205-225°C.). Its appearance under the microscope also showed it to be a mixture. The solid at 180°C. gave a sublimate which melted over a range. It was insoluble in sodium hydroxide, due perhaps to the formation of an insoluble salt, or to hydrolysis, if the acids are weak. A

copper wire test revealed the presence of bromine in the mixture. The solid insoluble in sodium carbonate was found to contain dibromo-fluoranthene (mixed melting point). Quinones prod uce a red colour with concentrated sulphuric acid and this test is a very delicate one. The solid gave no colour with sulphuric acid; oxidation to the quinone therefore does not take place.

Attempted Reduction of Dibromofluoranthene.

cf. von Braun (Ann., 1931, 488, 115).

Dibromofluoranthene (5 g.) was suspended in a solution of ethyl alcohol (100 c.c.) and water (25 c.c.). 4% sodium amalgam (160 g.) was added in portions to the briskly-stirred solution representing 20 atoms of sodium. Hydrogen was evolved and the mixture was left overnight at room temperature. The solution was decanted from the mercury and the solid separated by filtration. The alcohol filtrate was diluted with water and was discarded, since no precipitate was obtained. The solid was boiled with alcohol and filtered, m.p. 203°C. (mixed melting point with dibromofluoranthene, 205°C.). Thus no reduction had occurred, due perhaps to the insolubility of the dibromo-compound. The reaction was repeated; this time 20 c.c. of chloroform was added to facilitate solution, but no reduction occurred.

Nitration of dibromofluoranthene.

A modification of Fittig and Gebhard (Ann., 193, 147).

Dibromofluoranthene (1 g.) was added gradually to fuming nitric acid (3 c.c.), surrounded by iced water, at a rate such that the temperature of the mixture did not exceed 5°C. No subsequent heating on the water-bath was employed, as it was found that nitrous gases were evolved (i.e., oxidation was taking place). The solid was separated by filtration and was found to be insoluble in most solvents, including decalin and toluene. It was, however, very soluble in nitrobenzene, tetralin and xylene; but could not be crystallised from them or precipitated by the addition of benzene. The solid was boiled alternately with acetic acid and alcohol, when a constant melting point of 310°C. (with decomposition) was observed. Further purification was attempted by means of an aluminium oxide tower. A 1% solution of the solid in xylene was passed through a tower. The aluminium oxide assumed a buff colour. The xylene on evaporation left no residue, which showed that the compound had been adsorbed on to the aluminium oxide. The aluminium oxide tower was cut into sections determined by the colour distribution. Attempts were made to extract the solid with boiling xylene, or tetralin. After refluxing the solutions for 6 hours, no residue was left on evaporation of the filtrate. It was concluded that the solid was too strongly adsorbed on the aluminium oxide to be extracted.

The compound, m.p. 310°C., was then analysed for nitrogen and bromine. The results showed it to be tetranitrodibromofluoranthene.

Found: 10·3% nitrogen; 29·1% bromine.

$C_{16}H_4Br_2(NO_2)_4$ requires 10·38% nitrogen;
29·6% bromine.

The dibromofluoranthene was insoluble in concentrated sulphuric acid.

No nitration occurred when dibromofluoranthene was dissolved in acetic acid and fuming nitric acid was added.

Removal of bromine from dibromotetranitrofluoranthene.

Dibromotetranitrofluoranthene (·1 g.) was accurately weighed in a test tube provided with a ground glass stopper. Piperidine (4 c.c.) was added and the tube immersed in a thermostat at 46-48°C. for 24 hours. The contents of the tube were washed into a separating funnel with distilled water (50 c.c.) and shaken up with pure benzene to remove organic matter. The aqueous layer was removed into a bottle when almost colourless. 25 c.c. of silver nitrate accurately standardised, and 3 c.c. of dilute nitric acid were added. The mixture was shaken to coagulate the precipitated silver bromide. The excess of silver nitrate was titrated with potassium thiocyanate, ferric alum being used as indicator.

Results:

The silver nitrate solution was 0·0196 normal, and 10 c.c. $AgNO_3$ solution ≡ 9·25 c.c. KCNS solution. 0·1005 g. of compound required 7·5 c.c. of thiocyanate solution to neutralise the excess of silver nitrate solution used

∴ amount of $AgNO_3$, used = $(25 - 7{\cdot}5 \times \frac{10}{9{\cdot}25})$ = 16·9 c.c.

16·9 c.c. $AgNO_3$ ·0196 N ≡ $\frac{16{\cdot}9 \times 80 \times 0{\cdot}0196}{1000}$ ≡ 0·0265 g. Br

But 0·1005 g. compound contain $0{\cdot}1005 \times \frac{160}{540}$ = 0·02977 g. of bromine.

∴ % of bromine extracted is $\frac{{\cdot}0265}{{\cdot}02977} \times 100$ = 89%

Similar results were 88% and 88·5%. The incubation period was increased to 48 hours, but the results obtained was 90%.

Chlorination of fluoranthene with iodibenzene dichloride.

cf. Willgerodt (Ber., 1893, 26, 358)

Iodobenzene dichloride (10 g.), representing 1·1 molecular proportion, was added to fluoranthene (6 g.) dissolved in acetic acid (30 c.c.). The mixture was refluxed for three hours, when evolution of hydrochloric acid had ceased. The mixture was steam-distilled to remove acetic acid and iodobenzene. The residual solid was separated and recrystallised several times from acetic acid. Yellow needles, m.p. 176°, were obtained.

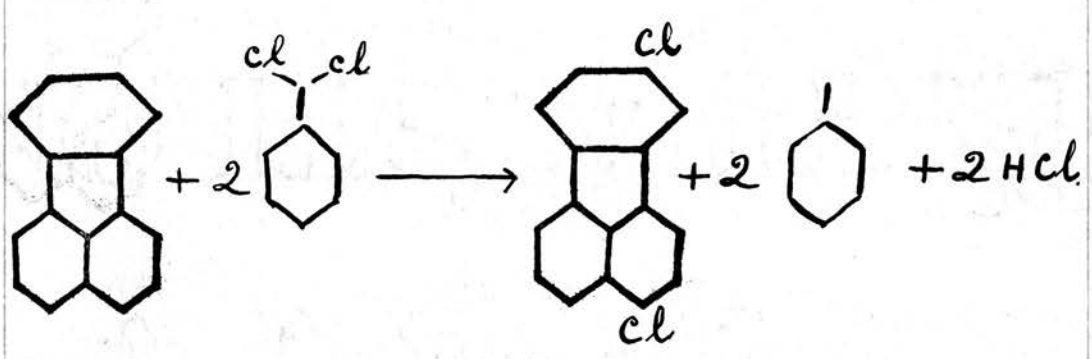
This compound readily sublimed at 165°C. to give yellow needles, m.p. 176°C. Yield, 1 g. As a result of analysis, these crystals were sho wn to be dichlorofluoranthene.

Found: 25·5% chlorine.

$C_{16}H_8Cl_2$ requires 26·2% chlorine.

Further purification of the solid was not possible. The picrate made from a sample of the residue melted at 170°C. Mixed melting point with fluoranthene picrate, 175°C. (melting point of fluoranthene picrate, 183°C.). The residue was thus shown to be chiefly fluoranthene. Yield 13%.

Equation for the reaction:



Nitration of dichlorofluoranthene.

The method was the same as that used in the nitration of dibromofluoranthene (page 63).

The solid obtained was boiled alternately with acetic acid and alcohol until a constant melting point of 280°C. was obtained. As a result of analysis, the compound was shown to be a tetranitrodichlorofluoranthene.

Found: 12·01% nitrogen.

$C_{16}H_4Cl_2(NO_2)_4$ requires 12·4% nitrogen.

Chlorination of fluoranthene in chloroform with chlorine.

Fluoranthene (10 g.) was dissolved in chloroform (50 c.c.) at 5°C. Chlorine gas was bubbled through the solution until a solid separated. The solid was recrystallised from acetic acid. No purification was effected. The solid was recrystallised four times from decalin, and then twice from toluene, when greenish-yellow needles, m.p. 295°C. (with decomposition), were obtained. This compound should be identical with that claimed by Goldschmidt (Monats., 1880, 1, 223) to be trichlorofluoranthene. Goldschmidt based his analysis on the formula $C_{15}H_7Cl_3$ and obtained 36·7% chlorine; calculated 36·3%. Based on the correct formula $C_{16}H_7Cl_3$ for the trichloro-compound, however, the percentage of chlorine is 34·9. This compound (m.p. 295°C.) was analysed for chlorine and the result showed it to be tetrachlorofluoranthene.

Found: 41·0% chlorine.

$C_{16}H_6Cl_4$ requires 41·6% chlorine.

Goldschmidt's alleged trichlorofluoranthene is tetrachlorofluoranthene. Any attempts to purify the residue resulted in the deposition of an oil.

Attempted preparation of tetrabromofluoranthene.

Since the compound, claimed by Goldschmidt (loc. cit.) to be a trichlorofluoranthene, was found to be tetrachlorofluoranthene, his work was repeated to ascertain whether the tribromofluoranthene was really a tetrabromofluoranthene. Goldschmidt's method was repeated, but his conclusions were not confirmed.

Repeat Goldschmidt's exper. Monats. I, 223.

A cold solution of bromine in acetic acid was added to a saturated solution of fluoranthene in acetic acid. No deposition of solid (in the cold or on heating), as claimed by Goldschmidt, was obtained, and only a trace of hydrobromic acid gas was observed. The compound isolated from the mixture was dibromofluoranthene, m.p. 205°C. (mixed melting point 205°C.). The experiment was repeated using specially dried reagents. The bromine was dried over phosphorous pentoxide and distilled, whilst the acetic acid was frozen out four times. Dibromofluoranthene was again isolated. Similar results were obtained when

(a) Iron filings were added as catalyst;

(b) The mixture was left for one week.

(c) 1 c.c. of water was added, as occasionally bromination proceeds in the presence of water more readily.

(d) Benzene was used as solvent in place of acetic acid.

Preparation of tetrabromofluoranthene.

Fluoranthene (1 g.) was directly added to excess bromine. A brisk reaction, followed by the evolution of hydrobromic acid gas, ensued. The mixture was heated on the water-bath to expel excess bromine. The residual solid was washed alternately with acetic acid and alcohol, and recrystallised several times from decalin. Yellowish-green needles, m.p. 302°C., were obtained. Yield theoretical.

As a result of a bromine analysis, the compound was found to be tetrabromofluoranthene.

Found: 62·4% bromine.

$C_{16}H_6Br_4$ requires 61·8% bromine.

Goldschmidt again based his analysis on the old formula of fluoranthene, i.e., $C_{15}H_{10}$.

A nitrogen analysis on trinitrofluoranthene itself was made, to make sure that it really was a trinitro-compound and not tetranitrofluoranthene. The result showed that it was indeed trinitrofluoranthene.

Found: 11·9% nitrogen.

$C_{16}H_7(NO_2)_3$ requires 12·17% nitrogen.

Bromination of Dibromofluoranthene.

Dibromofluoranthene (1 g.) was added in portions to bromine. The mixture was heated on the water-bath to remove excess bromine and hydrobromic acid. The residual solid was triturated under hot alcohol and

recrystallised from tetralin, when yellow needles, m.p. 302°C., were obtained. A mixed melting-point determination showed this compound to be identical with tetrabromofluoranthene, obtained by adding fluoranthene to excess bromine. The yield was quantitative. Tetrabromofluoranthene was insoluble in fuming nitric acid (hot and cold) and could not therefore be nitrated by this means. It was also insoluble in concentrated sulphuric acid.

The acetylation of fluoranthene.

cf. von Braun (Ann., 1932, 496, 184).

Fluoranthene (20 g.) was dissolved in carbon disulphide (120 g.), and powdered aluminium chloride (13·5 g.), one molecular proportion, was added to the ice-cold solution. Acetyl chloride (7·8 g.), one molecular proportion, was allowed to drop slowly into the well-stirred mixture. The mixture was stirred for two hours at room temperature and then refluxed on a water-bath for two hours. The evolution of hydrochloric acid gas was scarcely perceptible. Ice and dilute hydrochloric acid were cautiously added to remove excess of aluminium chloride, and then the carbon disulphide was evaporated. The residual oil, which gradually solidified on standing, was separated, washed and recrystallised from alcohol. Needles were obtained from the less soluble fractions by repeated recrystallisations from alcohol, melting at

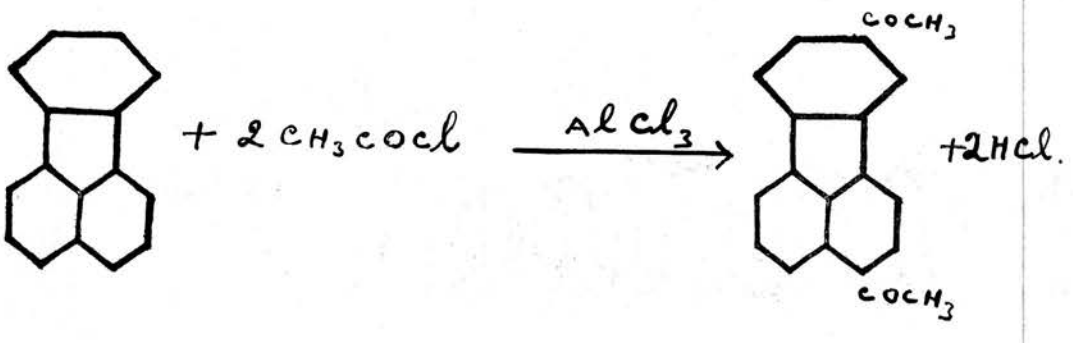
$C_{16}H_{10}$ = 202.
CH_3COCl = 78.
1 mol.

141°C. The results of analysis showed that this compound was diacetyl fluoranthene.

Found: carbon 83·65% ; hydrogen 5·15%.

$C_{16}H_8(COCH_3)_2$ requires carbon 83·9% ; hydrogen 4·90%.

A dinitrophenylhydrazone was made and was very insoluble in the normal solvents, including decalin and propionic acid. Diacetylfluoranthene in solution was found to emit a green fluorescence in ultraviolet light, whereas fluoranthene itself emits a blue fluorescence. The residual solid was found to be unchanged fluoranthene (mixed melting point and picrate). Yield, about 5%.



The acetylation was repeated, using two molecular proportions of aluminium chloride and acetyl chloride. The crude material isolated was very oily and when recrystallised from and alcohol and ether, melted over a range 60° to 90°C. Some diacetylfluoranthene was again isolated in the same way and the remainder of the solid was found to be very soluble in alcohol, acetic acid, etc. The filtrates were poured into water and the precipitate was separated by filtration. The solid was triturated with cold methyl alcohol. Hot

water was added to the boiling methyl alcohol filtrate until the liquid became cloudy. On cooling the solution, a pale yellow precipitate appeared which was filtered and dried. It melted over a range 60 to 80°C. Purification by recrystallisation was impossible, due to its ready solubility in all solvents. The dinitrophenylhydrazone was prepared. Successive recrystallisations from tetralin produced red needles melting at 293°C. Analysis showed this substance to be monoacetylfluoranthenedinitrophenylhydrazone.

Found: 13·10% nitrogen.

$C_{24}H_{16}N_4O_4$ requires 13·20% nitrogen.

The semicarbazone was prepared and successively recrystallised from butyl alcohol, when a pale yellow solid, m.p. 217-220°C., was isolated. This compound was shown to be monoacetylfluoranthenesemicarbazone.

Found: 13·61% nitrogen.

$C_{19}H_{15}N_3O$ requires 13·95% nitrogen.

The crude acetylfluoranthene and the semicarbazone also exhibited a green fluorescence.

The previous method was modified as follows:- three molecular proportions of acetyl chloride were added to the fluoranthene-carbon disulphide solution. Three molecular proportions of powdered aluminium chloride were added in portions at short intervals to the well-stirred mixture at room temperature. The oil obtained after removal of excess aluminium chloride did not solidify

and was therefore extracted with ether. The ether solution was dried and evaporated. Attempts to crystallise the oil from alcohol and ether failed, the oil being re-deposited. The oil was distilled in vacuo; the main portion distilled over at 265°C. and 11 mm. This oil was recrystallised successively from alcohol and was found to be diacetylfluoranthene, m.p. 141°C. Yield poor.

The acetylation was repeated using three molecular proportions of aluminium chloride and acetyl chloride. The resulting oil was distilled at 20 mm., a pale yellow oil distilling at 265°C. This was fractionally crystallised from methyl alcohol and yielded 2 g. of diacetylfluoranthene and 2 g. of a compound, m.p.85°C., which was shown to be acetylfluoranthene by analysis. Found: 87·9% carbon; 4·94% hydrogen.

$C_{18}H_{12}O$ requires 88·5% carbon; 4·92% hydrogen.

The monacetylfluoranthene was the more soluble. No further separation was obtained.

The attempted oxidation of diacetylfluoranthene.

cf. Arendonk and Cupery (J. Am. Chem. Soc., 1931, 53, 3184)

Diacetylfluoranthene (1 g.) was dissolved in chloroform (25 c.c.) and shaken up with 20% sodium hydroxide (20 c.c.) and a large excess of sodium hypochlorite freshly prepared by the action of sodium carbonate on bleaching powder. Vigorous shaking was

continued for 24 hours. Excess hypochlorite was removed by a stream of sulphur dioxide. The chloroform was removed and the solution, which must still be alkaline, was filtered. No acid was precipitated on acidifying the filtrate. The solid was purified and was found to be unchanged diacetylfluoranthene. Oxidation was not obtained when sodium hypobromite was used in place of the hypochlorite.

The attempted nitration of diacetylfluoranthene.

No nitration occurred when fuming nitric acid (5 c.c.) was added to a solution of diacetylfluoranthene in acetic acid. The nitration was attempted without a solvent. The solid, isolated after pouring the mixture into water, was shaken up with sodium carbonate solution. The insoluble fraction became too tarry to handle, while on acidifying the filtrate a very small amount of an acid was deposited. It was assumed that oxidation to phenols, etc. had occurred.

Attempt to brominate diacetylfluoranthene.

For method, see dibromination of fluoranthene (page 63). Bromination, however, did not occur, and unchanged diacetylfluoranthene was isolated, crystallising in plates (mixed melting point determination, and negative bromine test).

Nitration of acetylfluoranthene.

The method was the same as that used in the mono-nitration of fluoranthene (page 57). The solid obtained was recrystallised successively from tetralin, when a pale yellow solid, m.p. 220°C., with previous "sweating" was obtained. Since the compound was not pure, it was not analysed.

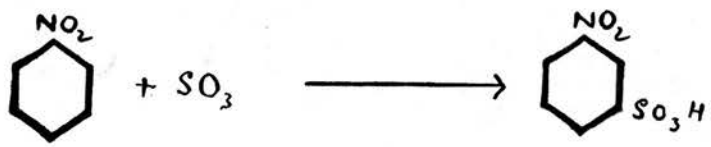
Attempted bromination of acetylfluoranthene.

The method was the same as that used in the dibromination of fluoranthene (page 60). The oily solid obtained was recrystallised from alcohol, but the oil was re-deposited. Ether was added to dissolve the oil but on evaporation of the ether at room temperature, an oily solid was obtained. Some of the solid was shaken up with alcoholic sodium hydroxide; a white precipitate was formed, which showed that bromination had occurred in the side chain.

D I S C U S S I O N.

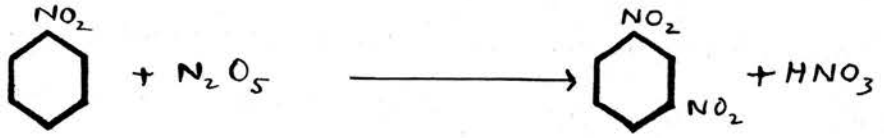
A considerable number of nitrations have been investigated involving nitric anhydride and various solvents. The practical points which arose out of the research will be detailed.

It is well known that sulphonation with sulphuric acid usually produces a mixture of isomers, whereas sulphonation with sulphur trioxide, which is the anhydride of sulphuric acid, often produces a quantitative yield of one particular isomer (Lauer, J. prakt. Chem., 1935, 143, 127). One object of this work was to ascertain whether similar results would be obtained in nitrations with the anhydride of nitric acid, i.e., nitrogen pentoxide. In the case of nitrations with this reagent a complication arises which does not occur in the corresponding sulphonation experiments. The reaction between sulphur trioxide and an organic compound consists merely in the addition of the sulphur trioxide to the compound: e.g., with nitrobenzene.



The reaction between nitrogen pentoxide and an organic compound proceeds with the liberation of 1 molecule of

nitric acid for every molecule of anhydride used: for example, in the case of nitrobenzene.



This nitric acid which is liberated may then react on the compound to produce a further quantity of nitro-compound: e.g., in the above example, dinitrobenzene. Nitric acid in its reactions on organic compounds generally produces a mixture of isomers, so that the by-product in the main reaction, which itself may be a nitrating agent, will no doubt influence the distribution of isomers of the resultant nitration product. Since nitrogen pentoxide is a much stronger reagent than nitric acid, the effect of the latter will be practically negligible. In spite of these considerations, however, one can definitely state that nitric anhydride does not lead to the formation of one isomer only, i.e., the para compound, because the percentages of the ortho-isomer which is formed are too high to be due to the nitric acid alone. The second question is: are the results obtained with nitrogen pentoxide and the mixed acids comparable? In view of the ease with which nitration occurs in solvents, such as sulphuric acid and acetic acid, it has been suggested that nitration is due to an anhydride such as $NO_2 \cdot O \cdot NO_2$ and

and $CH_3 \cdot CO \cdot O \cdot NO_2$ (e.g., Schaarschmidt, Z. angew. Chem., 1926, 39, 1457).

In order to facilitate a comparison, a table has been drawn up giving the results obtained by other authors for various nitrating reagents, as well as those obtained with nitrogen pentoxide, which are detailed in the experimental section of this thesis. All products given without a reference number were obtained in the course of this work. The table must be used with care, however, since the conditions of nitration are not standard throughout. Some nitrations were carried out at 0°C., some at higher temperatures, while for others the authors have not specified any conditions. Also some authors quote yields as percentages of the product isolated, and others as percentages of the theoretical yields based on the weight of starting material.

A table of results obtained by Gordon (Thesis, Edinburgh, 1937) is also included for comparison with the results obtained in this work.

Compound	N_2O_5 CCl_4	N_2O_5 CH_3COOH	N_2O_5 $(CH_3CO)_2O$	HNO_3	HNO_3 CH_3COOH	HNO_3 $(CH_3CO)_2O$	HNO_3 H_2SO_4	
Diphenyl	92% 4- 45℃	48% 4- 27% 2- 45℃	40% 4- 41% 2- 45℃	-	46-54% 4- 27-30% 2- (1) 70-90℃	-	57% 4- 33% 2- (2) 35-40℃	N_2O_4 No Solvent 100% 4- (13) 15℃
4-Nitro-diphenyl	71% 4:4'- 24% 2:4'- 45℃	64% 4:4'- 24% 2:4'- 45℃	36% 4:4'- 44% 2:4'- 45℃	63% 4:4'- 37% 2:4'- (3) 40-50℃	-	-	-	N_2O_4 CH_3COOH 4:4'- 2:4'- (13) 90-95℃
Diphenyl-methane	80% 4:4'- 13% 2:4'- 45℃	68% 4:4'- 12% 2:4'- 45℃	65% 4:4'- 28% 2:4'- 45℃	chiefly 4:4'- little 2:4'- (4) HEATED	-	-	2:4:2':4' Tetranitro (16) 15℃	N_2O_5 No Solvent 35·5% 4:4'- 25·5% 2:4'- 45℃
Fluorene	-	94% 2- 45℃	-	95% 2- (15)	79% 2- (5)	-	-	N_2O_4 No Solvent 70% 2- (13) 15℃
Acenaphthene	100% 4- 25℃	99% 4- 45℃	85·6% 4- 4·4% 2- 10℃	4:5 dinitro (7)	84% 4- (6) (7) 10℃	65-70% 2- 30-35% 4- (14) 138℃	N_2O_4 No Solvent 90-95% 4- (13) 15℃	Diacetylorthonitric acid 78% 4- 22% 2- (8) -5
Bromo-benzene	68% p- 28% o- 5℃	70% p- 17·6% o- 10℃	33% p- 8% o- 10℃	60% p- 40% o- (9) 10℃	59·4% p- 29·7% o- (9) 15℃	-	66% p- 31% o- (9) 15℃	N_2O_5 No Solvent 90% p- 4% o-
Nitrobenzene	NO NITRATION TAKES PLACE.			93·5% m- (10) 0℃			80-85-95% 95℃ 27℃ -14℃ (11)	N_2O_5 No Solvent 97% m- 45℃ Vol. changes N_2O_5 H_2SO_4 89-92% m-
m-Nitro-toluene	-	-	-	-	-	-	63% 3:4:6 30% 2:3:4 7% 2:3:6 (12) 50-120℃	N_2O_5 H_2SO_4 72% 3:4:6- 0-5℃

RESULTS obtained by Gordon (Thesis, Edinburgh, 1937.)

Compound	N_2O_5	CCl_4	N_2O_5	CH_3COOH	N_2O_5	$(CH_3CO)_2O$
Diphenyl	96%	4-	82·3%	4-	59·4%	4-
			17·7%	2-	40·6%	2-
Diphenylmethane	100%	4:4'-	-		-	
Fluorene	100%	2-	-		100%	2-
Acenaphthene	100%	4-	100%	4-	94·2%	4-
					5·8%	2-
Bromobenzene	100%	p-	-		-	
Nitrobenzene	100%	m-	-		-	

List of References.

1. Bell and Kenyon (J. Chem. Soc., 1926, 1242).
2. Jenkins, McCullough and Booth (J. Ind. Eng. Chem., 1930, 22, 32).
3. Gull and Turner (J. Chem. Soc., 1929, 494).
4. Staedel (Ann., 1878, 194, 363).
5. Kuhn (Org. Syntheses, 1933, 13, 74).
6. Sachs and Mosebach (Ber., 1911, 44, 2854).
7. Quincke (Ber., 1887, 20, 609).
8. Morgan and Harrison (J. Soc. Chem. Ind., 1930, 49, 413 T.)
9. Coste and Parry (Ber., 1896, 29,788).
10. Holleman (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 478).
11. Wyler (Helv. Chim. Acta, 1932, 15, 23).
12. Gibson, Duckham and Fairbairn (J. Chem. Soc., 1922, 121, 270).
13. Monte, Martello and Valente (Gazz. Chim. Ital., 1936, 66, 31).
14. Morgan and Sheasby (J. Soc. Chem. Ind., 1925, 44, 408 T.).
15. Anantakrishnan and Hughes, J. Chem. Soc., 1935, 1607).
16. Doer (Ber., 1872, 5, 795).

It is evident that the yield of the para isomer decreases when an active solvent is used in place of an inactive one in the following series:

$$CCl_4 > CH_3COOH > (CH_3CO)_2O$$

Pictet (Ber., 1907, 40, 1163) showed that nitric anhydride and acetic anhydride reacted to produce acetyl nitrate which is an energetic ortho-directing nitrating agent.

$$\begin{matrix} CH_3\ CO \\ CH_3\ CO \end{matrix}\!\!>\!O + O\!<\!\begin{matrix} NO_2 \\ NO_2 \end{matrix} \longrightarrow 2CH_3CO\cdot ONO_2$$

Francis (Ber., 1906, 39, 3798) prepared an analogous nitrate through the double decomposition involving benzoyl chloride and silver nitrate, which is also an ortho-directing nitrating agent.

$$C_6H_5COCl + AgONO_2 \longrightarrow AgCl + C_6H_5CO\cdot ONO_2$$

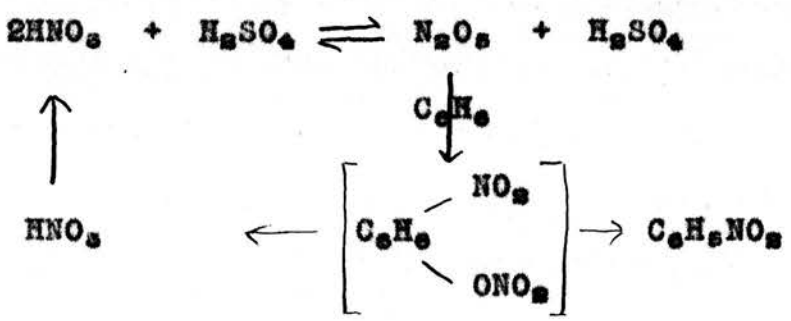
The above series then supports the work of Pictet if it be assumed that acetic acid reacts with nitrogen pentoxide to give some acetyl nitrate, but not as much as in the case of acetic anhydride. Thus with acetic acid we would expect the yield of the ortho-compound to be intermediate between the yields obtained with carbon tetrachloride and acetic anhydride - a fact which has been established. It seems quite definite that there are differences between nitrogen pentoxide and mixed acids as nitrating agents. Not only is the latter more powerful (e.g., nitration of nitrobenzene and diphenylmethane) but the relative quantities of isomers

formed are different in several instances (e.g., nitration of diphenyl).It is of interest to note that Morgan (loc. cit.) attributes the formation of 2-nitroacenaphthenein a nitration of acenaphthene with nitric acid and acetic anhydride to the anhydrous nature of the reaction. But in a nitration of acenaphthene in dry carbon tetrachloride with nitrogen pentoxide, which may also be termed anhydrous, a quantitative yield of 4-nitroacenaphthene was obtained. This result clearly shows that the formation of the 2-nitroacenaphthene in Morgan's experiment is not due to the absence of water, but to the presence of a solvent from which acetyl nitrate may be formed. The percentages of the ortho nitro-compounds quoted (loc. cit.) are very different from those recorded by Gordon. For example, the present author obtained 24% of 2:4'-dinitrodiphenyl and 13% of 2:4'-dinitrodiphenylmethane, where Gordon claims to have obtained 96% 4:4'-dinitrodiphenyl and 100% 4:4'-dinitrodiphenylmethane respectively. Similarly, 28% ortho bromonitrobenzene was obtained, where Gordon claimed to obtain 100% yield of the para compound. The other most striking difference is in the nitration of nitrobenzene in carbon tetrachloride. Gordon quotes a 100% yield of m-dinitrobenzene, whereas the author did not obtain nitration. The results obtained differ markedly from those of Haines and Adkins (loc. cit.) who claim to have obtained only para-bromonitrobenzene

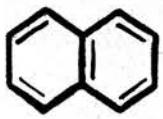
when bromobenzene was nitrated with nitrogen pentoxide in carbon tetrachloride, whereas we obtained 28% of the ortho isomer.

They could not nitrate benzoin acid under similar conditions, a result which was confirmed by us.

A study of the results obtained in the thermal analysis of the dinitrobenzenes has shown that the yield of the meta-compound varies with the temperature of nitration (see graph), low temperatures favouring the production of the meta-compound. Wyler (loc. cit.) shows that the same is true of nitrations with mixed acids. The sulphuric acid, as shown by the graph, affects the products of nitration; i.e., it is more than a solvent. It cannot act as a remover of water, as in the case of mixed acids, since the reaction is anhydrous. A possible explanation is that sulphonation first takes place, followed by the replacement of the sulphonic acid-groups by the nitro-groups, as in the formation of picric acid. It seems improbable, therefore, that the function of sulphuric acid in mixed acids is that of a dehydrater only, as represented in the following cycle:



McLeish and Campbell (J. Chem. Soc., 1937, 1103) showed that in naphthalene and hydrindene the double bond arrangement is



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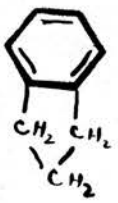
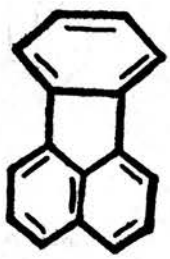
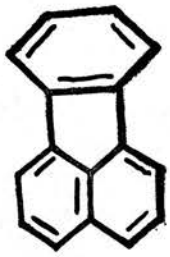


thus confirming the work of Fieser and Lothrop (J.A.C.S., 1936, 58, 2050). This suggests that fluoranthene may have the following double bond distribution:



In terms of the resonance theory we would expect that this structure makes the greater contribution to the resonance hybrid. Compare that used by von Braun who, however, gives no reason for this assignment of the double bonds.

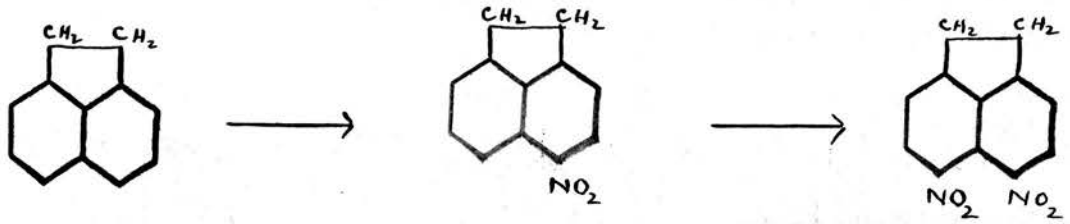


In subsequent pages spare formulae will be suggested which support formula I as the correct formula for fluoranthene. As already shown, substitution takes place primarily to position 4 and, to a lesser extent, to position 12. It seems reasonable to suppose that di-substitution will occur at positions 4 and 12. We can, then, advance a formula for trinitrofluoranthene:

Since the presence of a nitro-group in the ring tends to hinder further nitration in that ring, the third nitro-group will probably be in ring A. The 5-position

has been assigned for the following reasons:-

1. Acenaphthene nitrates first to the 4-position and, on further nitration, to the 4:5-positions (Morgan, loc. cit.)

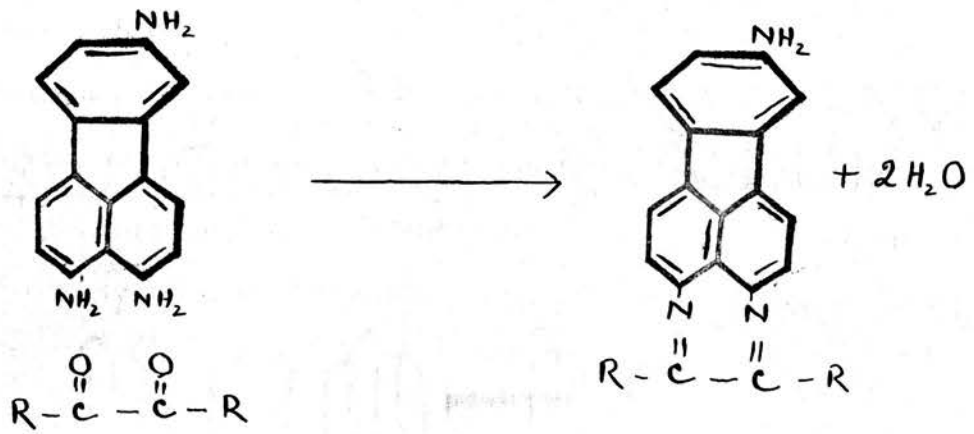


2. Schorygin and Toptschijew (Zentral., 1939, 2172) showed that the nitration of naphthalene with nitrogen peroxide proceeds at low temperatures to the α-nitro-compound. At higher temperatures, 1:5- and 1:8-dinitro-compounds are formed. In fluoranthene, however, the 5-position is blocked.

3. Beil and Kukl (Ann., 1873, 169, 88 ; 1880, 202,275) showed that the 1:8-dinitronaphthalene, like trinitrofluoranthene, is very stable towards oxidising agents. This evidence supports the structure advanced for trinitrofluoranthene, i.e., 4:5:12-trinitrofluoranthene. The fact that it is insoluble in all solvents, save concentrated nitric acid, no doubt explains its stability towards reducing agents. And the insolubility, together with the positions of the nitro-groups, explains its stability towards

oxidising agents.

If the reduction of trinitrofluoranthene to the triamino compound had been achieved we should have expected that this triamine would link up with a 1:2-diketone to give a quinoxaline derivative - i.e., if two amino-groups (and therefore the two nitro-groups) occupied ortho- or peri-positions, as is suggested.

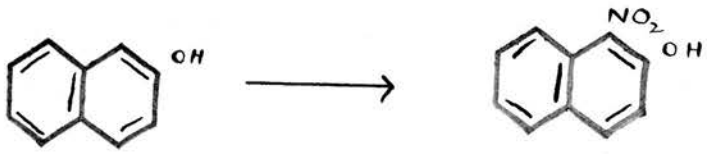


Mention may be made here of a simple yet effective method for introducing one nitro-group into the molecule. It consists in adding excess of fuming nitric acid, drop by drop, to a well-stirred saturated solution of the compound in acetic acid at a temperature not above 30°C. The nitro-compound, which is less soluble, is deposited and may be separated from unchanged compound. This method has been successfully applied

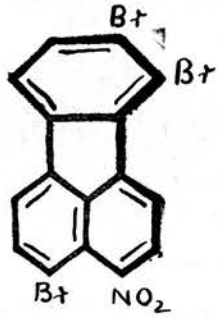
in the preparation of 4-nitrofluoranthene, and 4-bromo-12-nitrofluoranthene from fluoranthene and 4-bromo-fluoranthene respectively.

The fact that 4-nitrofluoranthene could not be brominated in solution, even after 24 hours at 60°C., shows that bromine substitution to the 12-position does not occur as readily as bromination to the 4-position. Direct bromination did produce a tribromonitrofluoranthene for which is suggested the following formula:-

This formula is in agreement with the proposed double bond distribution, if it be assumed that a double bond facilitates substitution; for example, β-naphthol yields on nitration 1-nitro-β-naphthol, and not 3-nitro-β-naphthol.



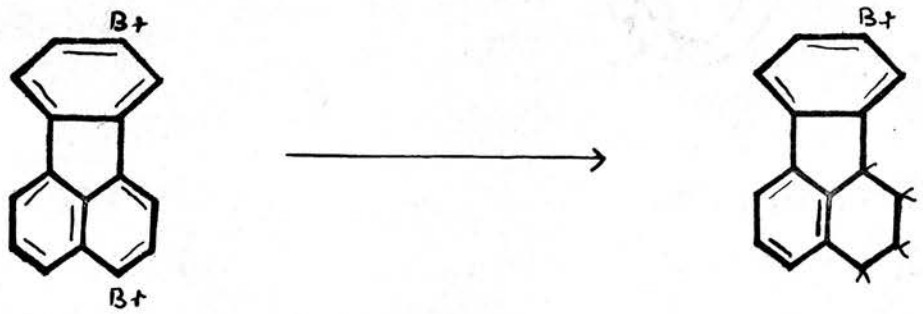
The alternative possibility for tribromonitrofluoranthene, however, cannot be overlooked.



A much improved method has been worked up for the mono-bromination of fluoranthene in which the yield is 70%. von Braun (loc. cit.) obtained 4-bromofluoranthene, along with dibromofluoranthene and unchanged fluoranthene. No dibromofluoranthene was detected with iodine bromide which is a weak reagent. The separation, therefore, of 4-bromofluoranthene was more readily achieved. 4-Bromofluoranthene was mononitrated in acetic acid to what is assumed to be 4-bromo-12-nitrofluoranthene (cf. 4-nitrofluoranthene which could not be mono-brominated). Attempts to introduce more nitro-groups into the molecule by direct nitration, and so to get a compound comparable with $C_{16}H_6Br_2O_8$, failed, as oxidation occurred. It was generally found that where nitration was effected by adding a compound to fuming nitric acid, considerable oxidation occurred as well.

This observation is supported by Bennett and Youle (Nature, 1938, 142, 356 ; J. Chem. Soc., 1938, 888 and 1818). These authors found that in the nitration of simple hydrocarbons, hydroxy by-products are formed. The phenomenon depends on the entry of a hydroxyl group according to the orientation law, followed by polynitration, and sometimes by the loss of the original substituent under the influence of the nitro-groups.

von Braun (loc. cit.) reduced 4-bromofluoranthene to tetrahydrofluoranthene. In the same way it was unsuccessfully attempted to reduce dibromofluoranthene to 12-bromotetrahydrofluoranthene. Failure must be attributed to the insolubility of dibromofluoranthene.



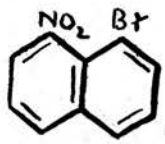
It was hoped that the reduced compound would be more readily oxidised to a known bromofluorenone carboxylic acid, thus providing confirmation of disubstitution to the 4:12-positions.

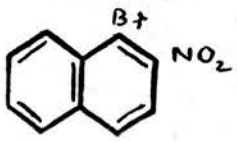
It is known that the presence of a nitro-group in the ortho- or para-position, with respect to a halogen

atom in the ring, causes the halogen to be activated. A halogen atom activated in this way may be readily removed by heating a solution of the substance in piperidine at 50°C. for some hours.

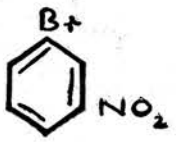
A nitro-group in the meta position does not activate a halogen.

In general, we may say that activation will occur only if the groups are separated by a double bond or system of conjugated double bonds. For example, 1-bromo-8-nitronaphthalene is not reactive, whereas 1-bromo-2-nitronaphthalene is reactive.

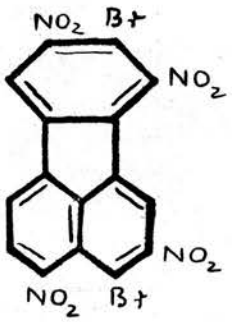




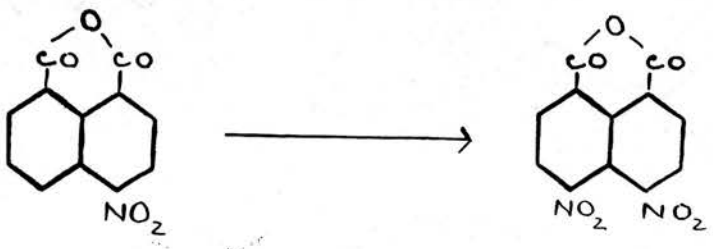
p-Bromonitrobenzene is reactive, whereas the meta-isomer is not reactive.



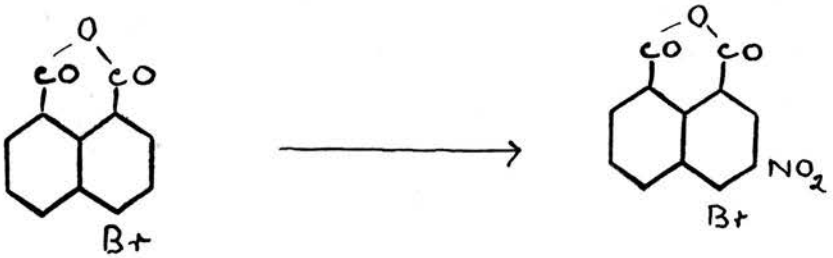
Dibromofluoranthene gave, on direct nitration, a dibromo-tetranitro compound. The ease with which both bromine atoms were removed from the molecule shows that they were activated, and therefore that the nitro-groups were situated in the ortho-positions with respect to the bromine.



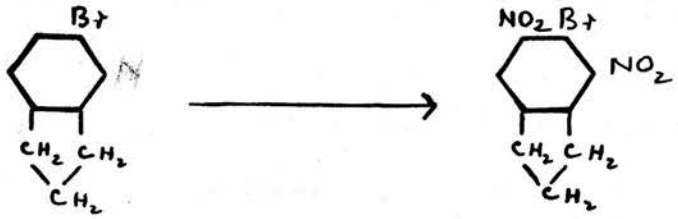
Evidence in support of this structure may be quoted from the work of Rule and Thompson (J. Chem. Soc., 1937, 1766). They found that nitration of 4-nitronaphthalic anhydride gave rise to 4:5-dinitronaphthalic anhydride,



whereas nitration of 4-bromonaphthalic anhydride yielded 4-bromo-3-nitronaphthalic anhydride.

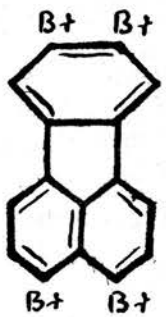


The authors unfortunately did not further nitrate this compound. Borsche and Bodenstein (Ber., 1926, 59, 1909) showed that 5-bromohydrindene on nitration with mixed acids gave 5-bromo-4:6-dinitrohydrindene.



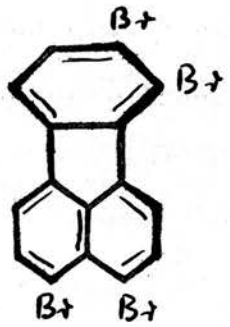
This evidence clearly supports the structure advocated, while again the double bond system advanced supports this view.

The following formula is suggested for the tetrabromofluoranthene obtained by direct bromination of fluoranthene or dibromofluoranthene:-



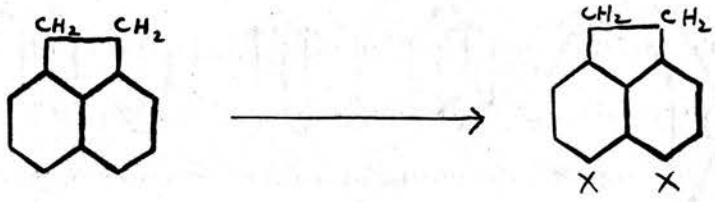
I

This is based on the double bond distribution assigned, though here, as in the case of tribromonitrofluoranthene, the following alternative is possible:-



II

The above formula (I) is also supported by the fact that acenaphthene dihalogenates to the 4:5-positions. Daschewski and Karischen (Zentral., 1939, 2416)



As has already been pointed out, this compound is listed in the literature as a tribromo compound (Goldschmidt, loc. cit.) - a conclusion not unnatural, since at the time fluoranthene was thought to be $C_{15}H_{10}$.

Dichlorofluoranthene, tetrachlorofluoranthene and dichlorotetranitrofluoranthene will presumably have formulae analggous to the corresponding bromo-compounds. Goldschmidt also reported tetrachlorofluoranthend as a

trichloro-compound.

The acetylation of fluoranthene gave rise to two new compounds - acetylfluoranthene and diacetyl-fluoranthene. As was pointed out (p. 12), von Braun (loc. cit.) showed that acylation proceeded first to the 12-position, so that we can designate these compounds 12-acetylfluoranthene and 4:12-diacetylfluoranthene. The yield in each case was very small and lack of material hampered comprehensive study.

An attempt to brominate the diacetyl-compound resulted in an inseparable mixture. It was shown, however, that the side-chain had been brominated, since bromine was removed by alcoholic potash. Schweitzer (Ber., 1891, 24, 547) showed that acetylnaphthalene brominated in the side chain under similar conditions.

SUMMARY Of DISCUSSION.

New methods have been worked up for mononitration and monobromination of fluoranthene, which may find a wide application. Errors appearing in the literature have been corrected. New compounds have been described and formulae suggested. And, finally, an orientation of trinitrofluoranthene has been suggested and evidence in support of this suggestion has been advanced.

In conclusion the author wishes to place on record his appreciation of Dr Campbell's advice and constant interest throughout the course of this work.
